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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME XI. INDUSTRIAL AND MUNICIPAL DISPOSAL CANDIDATE WASTE STREAM CONSTITUENT PROFILE REPORTS. ORGANIC COMPOUNDS (CONTINUED)

TRW Systems Group

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August 1973

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This volume contains summary information and evaluation of waste management methods in the form of Profile Reports for organic compounds. These Profile Reports were prepared for either a particular hazardous waste stream constituent or a group of related constituents. Each Profile Report contains a discussion of the waste stream constituents, their toxicology and other associated hazards, the definition of adequate management for the waste material, an evaluation of the current waste management practices with regard to their adequacy, and recommendation as to the most appropriate processing methods available and whether the waste material should be considered as a candidate for National Disposal, Industrial Disposal, or Municipal Disposal.

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Industrial Disposal Candidate
Municipal Disposal Candidate
Hazardous Wastes
Ethers
Derivatives of Benzene
Glycols
Nitro-Organo Compounds
Polychlorinated Biphenyls
Organo-Halides
Tetraethyl- and Tetramethyllead
Phosgene
Alkyl Halides
Halogenated Aliphatic Hydrocarbons
Quinone
Chloropicrin
Benzoyl Peroxide
Cyanuric Triazide
Hydrazine
Maleic Anhydride
Nitroaniline
Oxalic Acid
Tricresyl Phosphate

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Volume XI. Industrial and Municipal Disposal Candidate Waste Stream Constituent Profile Reports - Organic Compounds (Continued)

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The Solid Waste Research Laboratory of the National Environmental Research Center - Cincinnati, U.S. Environmental Protection Agency has reviewed this report and approved its publication. Approval does not signify that the contents necessarily reflect the views and policies of this Laboratory or of the U.S. Environmental Protection Agency, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
National Environmental Research Center
Cincinnati, Ohio

TABLE OF CONTENTS

VOLUME XI

INDUSTRIAL AND MUNICIPAL DISPOSAL CANDIDATE WASTE STREAM CONSTITUENT PROFILE REPORTS

Organic Compounds - Continued

Page

Benzoyl Peroxide (514) 1

1,2,4-Butanetriol Trinitrate (BTTN) (515) 9

Chloropicrin (111) 15

Cyanuric Triazide (519) 21

Diethylether (152), Dioxane (153), Ethers (174), Ethylene Glycol Monoethyl Ether (187), Ethylene Glycol Monoethyl Ether Acetate (188), Isopropyl Ether (232), Polypropylene Glycol Methyl Ether (339), Propylene Oxide (362), Tetrahydrofuran (426) 27

Dinitrobenzene (163) 43

Dinitrophenol (164) 51

Diphenylamine (167) 63

Ethylene Bromide (182), Methyl Bromide (267), Methyl Chloride (268) . 69

Ethylenimine (190) 91

Glycerol Monolactate Trinitrate (GLNT) (524) 99

Hydrazine Azide/Hydrazine (527) 105

Hydroquinone (220) 111

Maleic Anhydride (249) 119

Manganese Methylcyclopentadienyltricarbonyl (502) 127

Nitroaniline (300) 137

Nitrobenzene (301) 145

Preceding page blank

TABLE OF CONTENTS (CONTINUED)

Page

meta- and para-Nitrochlorobenzene (302) 153

Nitroethane (303), Nitromethane (308), 1-Nitropropane (311) 161

4-Nitrophenol (310), 4-Nitrotoluene (312) 173

Oxalic Acid (317) 183

Phosgene (Carbonyl Chloride) (329, 101) 191

Polychlorinated Biphenyls (507) 199

Polyvinyl Nitrate (PVN) (535) 219

Quinone (365) 223

Tetraethyl- and Tetramethyllead (425,427) 229

Tetranitromethane (428) 241

Tricresyl Phosphate (440) 247

PROFILE REPORT

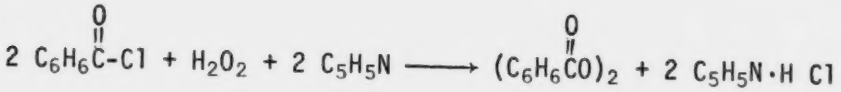
Benzoyl Peroxide (514)

1. GENERAL

Introduction

Benzoyl peroxide was first synthetized by B.C. Brodie in 1859. Commercial use began in the early 1900's when it was found that benzoyl peroxide was an effective bleaching agent for edible oils, and somewhat later, an excellent bleach for flour. Today, its major use is as a polymerization initiator for such polymers as polyethylene, polyvinyl chloride, polystyrene, polyester thermosets, polyacrylates, styrene-butadiene rubber and many others.[1433]

Benzoyl peroxide is prepared by treating benzoyl chloride with sodium peroxide or hydrogen peroxide in the presence of base such as pyridine or sodium hydroxide.



$$2\ C_6H_6\overset{O}{\overset{\|}{C}}\text{-}Cl + H_2O_2 + 2\ C_5H_5N \longrightarrow (C_6H_6\overset{O}{\overset{\|}{C}}O)_2 + 2\ C_5H_5N\cdot H\ Cl$$

Major manufacturers of benzoyl peroxide are:[1718,1790]

Penwalt Corp., Lucidol Div.,
1740 Military Rd., Buffalo, New York

Reichold Chemicals, Inc.
RCI Building, White Plains, New York

Tenneco Chemicals, Inc.
Modex Div., P.O.Box 2, Piscataway, New Jersey

U.S. Pexoggen, Div.Argus Chemical Corp.
850 Morton Ave, Richmond, California

Physical and Chemical Properties

The physical and chemical properties of benzoyl peroxide are included in the attached worksheet.

2. TOXICOLOGY[0766,2351,2380]

The physiological effects of benzoyl peroxide have not been fully determined, therefore extra care should be exercised in its handling. Local effects include irritation, particularly to the eyes, nose and throat. The nature of systemic effects has not been investigated. A Threshold Limit Value (TLV) of 5 mg/M^3 has been established.

3. OTHER HAZARDS

Benzoyl peroxide may decompose explosively when subjected to heat, shock or electrical discharge. The presence of organic material in benzoyl peroxide increases the hazard. Molten material will decompose instantly and explosively. Benzoyl peroxide is a powerful oxidizer and polymerization initiator, thus it can react with reducing agents and monomers to cause fire or explosion. These materials include alcohols, amines, various organic and inorganic acids, organic monomers and polymerization accelerators.[0766,1433,2380]

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation

Benzoyl peroxide is packed in 1-lb or smaller fiber or paper containers that are either taped or glued shut. These are packed for shipment in wood or fiberboard boxes with each container surrounded by asbestos or fire-resistant cushioning of equal efficiency. Net weight of contents must not exceed 50 lb.[2380]

Benzoyl peroxide is also shipped with 30 to 50 percent water by weight since the addition of water considerably reduces all hazards. This material is packed in wood boxes containing polyethylene lined paper bags or aluminum drums with a maximum 1 lb dry weight capacity. Maximum gross weight must not exceed 200 lb. Wet material is also shipped in metal drums with polyethylene liners with a maximum gross weight of 350 lb.[0766,2380]

Shipping containers must have a Department of Transportation (DOT) yellow Oxidizing Material label and preferably an approved MCA warning label. Trucks carrying over 2,500 lb gross weight of material must be marked "DANGEROUS". The same label must be applied to rail cars carrying one or more packages of benzoyl peroxide.[2380]

Benzoyl peroxide is friction-, impact-, spark- and heat-sensitive. In addition, it is capable of reacting violently with many organic compounds. Thus,wooden boxes and metal containers should be opened with spark-resistant tools and only non-metallic instruments should be used to open fiber or paper containers. The material should be kept away from all sources of heat and electrical discharge. Grinding should only be done with extreme care with the proper diluents. Spills should be wiped up immediately with a soft brush or broom.[0766,2351,2380]

When storing benzoyl peroxide, all reasonable precautions must be taken to guard against fire and explosion hazards. It should be stored in minimum amounts in a cool place, out of direct rays of the sun, away from sparks, open flames and other sources of heat. Storage should be isolated from possible contact with acids, alcohols, ethers or other reducing agents or polymerization catalysts. Wet benzoyl peroxide must not be allowed to dry out.[0766,2380]

Use/Disposal

Benzoyl peroxide is used as a catalyst in various organic reactions and as a bleaching agent for oils and flour. The amounts used are normally very small in relation to the amount of the other materials. The by-products of reaction, usually benzoic acid, are not usually removed.[1433,2380]

Empty containers are normally examined to make certain that no material remains and then, if necessary, flushed with water to remove any residue and kept wet until they can be disposed of by incineration in an open incinerator. Waste benzoyl peroxide is stored wet until it can be destroyed with about ten times its weight of 10 percent sodium hydroxide solution. The reaction is only mildly exothermic and the final product, benzoic acid and sodium benzoate may be flushed into the

The safe disposal of benzoyl peroxide is defined in terms of recommended provisional limits for that material in the environment. The recommended provisional limits are as follows:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Benzoyl peroxide in air	0.05 mg/M^3	.01 TLV
Benzoyl peroxide in water and soil	0.25 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF DISPOSAL PROCEDURE

Option No. 1 - Disposal of Empty Containers by Incineration

All cartons and bags should be examined to ascertain that they contain no residual benzoyl peroxide. Residual material, if present, should be flushed out with water. The empty cartons should be crushed and placed in a special collection drum. Keeping the contents of the drum moist is a good safety precaution. Periodically, the contents of the drum should be carefully incinerated.

Option No. 2 - Decomposition with Sodium Hydroxide

Unusable benzoyl peroxide is best stored wet until disposal. The slurry of waste material can be destroyed safely and easily by adding it slowly with stirring to ten times its weight of 10 percent sodium hydroxide solution. The reaction is only mildly exothermic. The final solution containing sodium benzoate and benzoic acid, both biodegradable,[1543] may be flushed into the drain. Disposal of large quantities of solution may require pH adjustment before release into the sewer.

Option No. 3 - Mixing with a Noncombustible material and Incineration

An equal weight of noncombustible material such as vermiculite or perlite can be added to a slurry of benzoyl peroxide. The excess water is then filtered off and the wet paste is carefully burned in a slurry bed, auxiliary fired incinerator. This method is suitable only if quantities of material are small and the incinerator is equipped with particulate removal equipment to insure against noncombustibles being discharged to the atmosphere.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Due to the hazards of shipping benzoyl peroxide and considering the ease with which wastes can be destroyed at the site of generation, this compound should not be considered a candidate waste stream constituent for the National Disposal Site.

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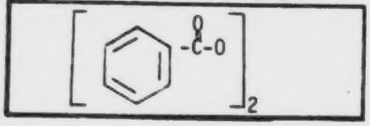
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Benzoyl peroxide (514)

IUC Name ______

Common Names dibenzoyl peroxide, benzoyl super oxide, Lucidol.

Structural Formula



Molecular Wt. 242.22 Melting Pt. 103-105 C(1) Boiling Pt. decomposes(1)

Density (Condensed) 1.3340 @ 25 C(3) Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. 176 F(1)

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water insoluble(2) Hot Water ______ Ethanol slightly(2)

Others: soluble in benzene, acetone, chloroform(2)

Acid, Base Properties neutral to slightly acid due to residual HCl(3)

Highly Reactive with reducing agents possibly resulting in fire(1,3)

Compatible with ______

Shipped in ______

ICC Classification Yellow-Label Oxidizing Material Coast Guard Classification yellow label

Comments may explode spontaneously; shock and friction sensitive(1,3)

References (1) 0766
(2) 1492
(3) 2380

PROFILE REPORT

1,2,4-Butanetriol Trinitrate (BTTN) (515)

1. GENERAL

BTTN is a liquid at room temperature that is a good gelatinizer for nitrocellulose. BTTN has been evaluated in the United States as a plasticizer for nitrocellulose but has not been used to any extent in this country. During World War II the Germans used BTTN to gelatinize nitrocellulose. BTTN is prepared by nitrating 1,2,4-butanetriol.[2169]

The physical/chemical properties for BTTN are summarized in the attached worksheet.

2. TOXICOLOGY

Because of its solubility in water and organic solvents which permits absorption, BTTN is more of a health problem than many of the other compounds containing nitro ester groups. BTTN can cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure, central nervous system depression, coma and respiratory paralysis through ingestion, inhalation or skin adsorption.[0766]

The Threshold Limit Value (TLV) for BTTN has not been established, but should be the same as that recommended for nitroglycerin- 0.2 ppm. Waste forms containing BTTN would probably consist of small experimental lots of explosive or military munitions made with the explosive on an experimental basis.

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3. OTHER HAZARDS

BTTN is a powerful explosive whose decomposition into gaseous products is accompanied by the evolution of large quantities of heat and a shock wave. BTTN is very sensitive to heat, friction and spark. Its impact sensitivity is about the same as for nitroglycerin (2 Kg weight, 15 cm with Bureau of Mines apparatus).[1147, 2169] The Brisance by Sand Test gives about the same results as nitroglycerin; 49 g vs 51.5g for nitroglycerin. The explosion temperature, 5-sec value, for BTTN is 230 C vs 220 C for nitroglycerin. It is more stable than nitroglycerin.[2169]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Details concerning manufacturing processes and waste streams from the manufacture of BTTN have not been found in the literature, but laboratory instructions for its preparation indicate that BTTN, if manufactured, would be prepared by the same processes as nitroglycerin and these processes would have similar waste streams. Details of nitroglycerin manufacture, handling and storage requirements are given in the Profile Report on Nitroglycerin (307). Because BTTN has about the same sensitivity to impact, heat and friction as nitroglycerin, it can be assumed that BTTN will not be transported beyond the plant in which it is manufactured. No BTTN should be discharged in a waste stream because of the explosive hazard created.

The safe disposal of BTTN is defined in terms of the recommended provisional limits in the atmosphere, and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
BTTN	0.02 mg/M^3	0.01 TLV*

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
BTTN	0.1 mg/l*	Stokinger and Woodward Method

*Estimated

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

BTTN collected from spills and catch tanks, or considered unsuitable for use, should be disposed of by careful burning after absorption in sawdust, wood pulp or fullers earth. If BTTN is spilled on the ground, the contaminated ground should be removed with low impact tools and burned. Ignition of BTTN is usually accomplished by igniting a black powder squib placed on the surface. All burning is performed in a remote area.[1142] Although the products of combustion contain considerable NO_x, processes to control pollution from the products of combustion or BTTN and similar compounds are not in wide use.

Investigations are being conducted to develop better methods for the disposal of BTTN and similar compounds, including nitroglycerin, than the open-burning techniques currently used. These methods are based upon the use of scrubber-equipped incinerator systems for the controlled burning of explosive wastes, but this method is not available for wide use at this time. Additional research is required.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

BTTN is not normally a candidate waste stream constituent for National Disposal Sites because it is not safe to transport, and facilities for its disposal are available at the sites where it would be manufactured. Disposal of BTTN at these facilities by open-burning is not a satisfactory technique. Controlled incineration in scrubber-equipped systems is recommended for disposal of BTTN wastes and waste gelatinized nitrocellulose containing BTTN. The BTTN wastes should be handled by a qualified ordnance disposal team.

7. REFERENCES

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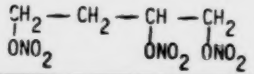
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 1,2,4-Butanetriol trinitrate (515)

IUC Name 1,2,4-Butanetriol trinitrate

Common Names BTTN

Structural Formula



$$\underset{ONO_2}{CH_2}-CH_2-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$$

Molecular Wt. 231.06(1) Melting Pt. ____ Boiling Pt. ____

Density (Condensed) 1.52g/cc @ 20 C(1) Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water slightly soluble Hot Water ____ Ethanol miscible

Others: miscible with ether, acetone, and 2:1ether-ethanol

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Not shipped Coast Guard Classification Not shipped

Comments

References (1) 2169

PROFILE REPORT

Chloropicrin (111)

1. GENERAL

Chloropicrin is a slightly oily, colorless liquid boiling at 112 C and solidifying at -69 C. It is a powerful irritant and affects all body surfaces. It causes lachrymation, vomiting, bronchitis, and pulmonary edema.[766]

This material is primarily used as an insecticide and parasiticide[1492] for disinfecting cereals and grains. It is called vomiting gas and has been extensively used by the military as a war gas.[0766]

Chloropicrin is made by the chlorination of nitromethane in the presence of calcium carbonate, or by the reaction of picric acid with sodium hypochlorite.[1316] It is also produced commercially by reacting sodium hypochlorite with nitromethane.[1749]

Commercial facilities for the manufacture of chloropicrin are operated by Dow Chemical Company[1718], International Minerals & Chemical Corporation[1718], Niklor Chemical Co., Inc.[1749] and Sobin Chemical Incorporated.[1750]

2. TOXICOLOGY[0766]

Chloropicrin is a powerful irritant and affects all body surfaces. It causes lachrymation, vomiting, bronchitis, and pulmonary edema. A concentration of 1 ppm causes a smarting pain in the eyes and therefore, in itself constitutes a good warning of exposure. It causes vomiting, probably due to swallowing saliva in which small amounts of chloropicrin have dissolved. Its primary lethal effect is to produce lung injury and it is a difficult gas to protect oneself against because it is chemically inert and does not react with the usual chemicals used in gas masks.

3. OTHER HAZARDS

Four parts per million chloropicrin in air is sufficient to render a man unfit for action and 20 ppm, when breathed from one to two minutes, causes definite bronchial or pulmonary lesions. Chloropicrin emits highly toxic fumes when heated to decomposition.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Gloves and chemical goggles should be worn to protect the skin and eyes when handling chloropicrin. If it is necessary to be in discomforting concentrations of chloropicrin vapor, a full face gas mask with a canister recommended for use in acid gases and organic vapors should be worn.

Chloropicrin is shipped as pure material and as mixtures with nonflammable, nonliquified compressed gas, and mixtures containing no compressed gas. Regulations covering the shipping of these materials are found in Federal Code of Regulations.[0278] Glass and steel containers are suitable for shipping chloropicrin. Containers and handling equipment made of aluminum, magnesium or their alloys should not be used in chloropicrin service as under certain conditions these materials are severely corroded.

Chloropicrin should be stored in tightly closed containers in a cool place away from any dwellings. In outside storage, drums should be stored on their sides to prevent water from collecting around the bungs.

Disposal/Reuse

A definition of acceptable criteria for the disposal of chloropicrin must also take into account acceptable criteria for the release of hydrogen chloride, hydrochloric acid and nitrogen oxides to the environment, since current practice in chloropicrin disposal involves some processes that reduce chloropicrin to these materials.

Current techniques utilize incineration, land burial and lagooning. The recommended provisional limits for chloropicrin, hydrogen chloride, hydrochloric acid, and nitrogen oxides in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis of Recommendation
Chloropicrin in air	0.001 ppm (0.007 mg/M^3)	0.01 TLV
Hydrogen chloride in air	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Hydrochloric acid in air	0.05 ppm (0.02 mg/M^3)	0.01 TLV
Nitrogen oxides in air	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Chloropicrin in water and soil	0.035 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Chloropicrin is expected to appear primarily as dilute aqueous and organic waste streams and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Chloropicrin

In the event it became necessary to dispose of a significant quantity of concentrated chloropicrin, two disposal options are available. The first option is to contact the manufacturer and determine if it is possible to return the materials. Niklor Chemical Company,[1749] and Sobin Chemical Incorporated,[1750] have indicated that recycling of chloropicrin is possible, depending on the contaminating material. The second option is incineration but since chloropicrin is nonflammable, it must be added to fuel or sprayed into an incinerator at high temperatures. It is expected that a liquid combustor followed by secondary combustion and aqueous or caustic scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second. The abatement problem may be simplified by insuring against elemental chlorine formation through injection of steam or the utilization of methane as a fuel in the combustion process. Both options provide adequate ways to handle the concentrated waste but it is strongly recommended that recycling be used whenever possible.

Dilute Aqueous Waste

Dilute aqueous waste containing chloropicrin is lagooned and allowed to gas off,[1750] or is incinerated with scrubbers to remove the hydrogen chloride from the effluent gas.[1772] It is recommended that the material to be lagooned be reacted with sodium sulfite or sodium bisulfite to suppress the noxious properties of the chloropicrin and any resulting sludge be incinerated or buried in an approved California Class I type landfill. Both lagooning and incineration are adequate means of disposing of chloropicrin provided the concentrations released to the environment do not exceed the provisional limits.

Dilute Organic Waste

Dilute organic waste generated during the manufacture of chloropicrin are disposed of either by land burial,[1750] or incineration.[1772] .Incineration with proper treatment of the effluent gas to remove hydrogen chloride and nitrogen oxides is the primary option for disposing of dilute organic waste. An alternate method of disposal would be in an approved chemical California Class I type landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Chloropicrin is expected to appear primarily as dilute organic and aqueous wastes, and to a much lesser degree as concentrated waste. Facilities for handling the disposal of these wastes are located at manufacturing sites and industrial disposal facilities and represent common industrial techniques. This material is not judged to be a candidate waste stream constituent for National Disposal Sites.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Chloropicrine (111)

IUC Name Nitrotrichloromethane(1)

Common Names Chloropicrin(1), Nitrochloroform(1)
Trichloronitromethane

Structural Formula

Cl_3CNO_2

Molecular Wt. 164.38(1) Melting Pt. -64 C(1) Boiling Pt. 112^{757} C(1)

Density (Condensed) 1.6558 @ 2014 C Density (gas) 5.69(4) @

Vapor Pressure(2) (recommended 55 C and 20 C)

18.3 mm @ 25 C 40 @ 33.8 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.16% @ 20 C(2) Hot Water Ethanol Soluble(1)

Others: Soluble in acetone(1), benzene(1), methanol(1), Acetic acid(1), ether(3)

Acid, Base Properties May be corrosive under certain conditions.

Highly Reactive with

Compatible with Fuel oil, kerosene

Shipped in Glass, steel containers and in steel containers as nonliquified compressed gas6

ICC Classification Poison A(4) Coast Guard Classification Poison A(4)

Comments Non-flammable(5)

References (1) 1570 (4) 0766
(2) 1618 (5) 0509
(3) 1492 (6) 0278

PROFILE REPORT
Cyanuric Triazide (519)

1. GENERAL

Cyanuric triazide is a powerful initiator in which azide groups are combined with a heterocyclic ring. First step in preparation is the reaction of chlorine and hydrogen cyanide to form cyanuric chloride, a trimer. Upon reaction of cyanuric chloride with sodium azide in an aqueous solution at room temperature cyanuric triazide is formed. Cyanuric triazide has initiating properties that are stronger than those of mercury fulminate. It is highly dangerous to handle and sensitive to impact and friction; it has been known to explode during manufacture. Large crystals, which explode even under the pressure of a rubber stopper are particularly dangerous. Its sensitivity accounts for the fact that the substance has found no practical application.[2171]

The physical/chemical properties for cyanuric triazide are summarized in the attached worksheet.

2. TOXICOLOGY

The toxicity of cyanuric triazide is unknown, but upon acidification toxic fumes are liberated.[0766] The liberated fumes probably contain hydrazoic acid which, in the concentration range of 0.7-7.0 mg/m^3, evokes marked symptoms of intoxication (see Profile Report on Hydrazoic Acid, [528]).

3. OTHER HAZARDS

Cyanuric triazide is a detonating agent that is so sensitive to heat, impact and friction that it undergoes detonation when subjected to a flame or percussion. Its ignition temperature, when heated at a rate of 20 C/min., is 205 to 208 C but decomposition becomes evident on heating at a temperature slightly exceeding 100 C. It is exploded by an impact energy one-third of that which detonates mercury fulminate.[2171]

Because cyanuric triazide is so dangerous to handle and sensitive to impact and friction, it has found no practical application, and it is not manufactured or shipped.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Cyanuric triazide does not produce NO_x as a decomposition product when detonated. For this reason, and because only small, experimental quantities are synthesized, cyanuric triazide laboratory wastes and scrap should be collected and detonated in a suitable remote destruction pit area. Provisional limits for cyanuric triazide have not been established.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Cyanuric triazide is at present not being manufactured and, therefore, specific disposal procedures are not published. If in the future it should become necessary to dispose of cyanuric triazide, the method recommended in the Ordnance Safety Manual for the disposal of initiating explosives could be used with care, if employed by an ordnance disposal team experienced in handling initiating explosives. When using the recommended procedure, bags containing the explosive,wet with water, are carried to a destruction pit, placed in intimate contact with each other, and a blasting cap placed between the bags to initiate the explosives. All remaining explosives should be kept behind a barricade with overhead protection during destruction operation. Personnel in the area should remain behind a similar barricade.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

There is no commercial production at present of cyanuric triazide, and provisions exist for its destruction at most arsenals and explosive manufacturing plants which produce the material experimentally. Any cyanuric triazide wastes not destroyed at such facilities are candidates for National Disposal Sites, if safe to handle and transport. The waste should be transported wet, in a vehicle properly equipped for safe transport of initiating explosives, and only to the nearest satisfactory disposal site. The process to be employed at the site should be detonation, as cited in Section 5. The wastes should be handled and transported only by a qualified ordnance team, experienced in handling sensitive initiators. If the wastes are unsafe to handle or transport to the National Disposal Site, they should be detonated at the nearest safe cleared area.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cyanuric Triazide (519)

IUC Name

Common Names

Structural Formula

$(CN)_3\ (N_3)_3$

Molecular Wt. 96 (1)

Melting Pt. 100 C decomposes (1)

Boiling Pt.

Density (Condensed) @

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

slightly volatile

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble (1)

Hot Water Sparingly soluble (1)

Ethanol soluble (1)

Others: Soluble-acetone, benzene, ether (1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in not shipped (1)

ICC Classification None (1)

Coast Guard Classification none (1)

Comments

References (1) 2171

2

PROFILE REPORT

Diethylether (152), Dioxane (153), Ethers (174), Ethylene Glycol Monoethyl Ether (187), Ethylene Glycol Monoethyl Ether Acetate (188), Isopropyl Ether (232), Polypropylene Glycol Methyl Ether (339), Propylene Oxide (362), Tetrahydrofuran (426)

1. GENERAL

Introduction[1433]

Ethers are compounds of the type R-O-R' where R and R' may be the same or different alkyl or aryl radicals. Ethers resemble the corresponding hydrocarbons in chemical reactivity, provided there are no additional, more reactive functional groups present. On prolonged exposure to air, ethers autooxidize to peroxides, which can be dangerously explosive.

Manufacture[1433]

Catalytic Dehydration of Alcohols - This preparative method is used principally for the production of simple ethers (e.g., ethyl ether). The reaction usually involves several of the reaction steps outlined below, the particular combination of steps employed is governed by the identity of the desired product.

$$\mathrm{ROH} + \mathrm{HOSO_2OH} \xrightarrow{\text{Cold}} \mathrm{ROSO_2OH} + \mathrm{HOH}$$

$$\mathrm{ROSO_2OH} + \mathrm{ROH} \xrightarrow{\Delta} \mathrm{ROR} + \mathrm{H_2SO_4}$$

$$\mathrm{ROSO_2OH} + \mathrm{ROH} \xrightarrow{\Delta} \mathrm{ROSO_2OR} + \mathrm{HOH}$$

$$\mathrm{ROSO_2OR} + \mathrm{ROH} \xrightarrow{\Delta} \mathrm{ROR} + \mathrm{ROSO_2OH}$$

Williamson Ether Synthesis - The Williamson ether synthesis may be used to prepare either simple (R=R') or mixed ethers (R≠R').

$$\mathrm{RBr} + \mathrm{NaOR'} \longrightarrow \mathrm{ROR'} + \mathrm{NaBr}$$

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Uses and Application[1433,2401]

The principal applications of ethers are as solvents for organic reactions and extractions, as plasticizers, as vehicles for other products and as anesthetics. Ethers are insoluble in water, but are solvents for many organic compounds, and therefore, have found wide application in paint and varnish removers, as high-boiling solvents for gums, resins and waxes, and in lubricating oil. The vapors of certain ethers are toxic to insects and are useful as agricultural insecticides and industrial fumigants.

Diethylether - Ethyl ether is a good solvent or extractant for fats, waxes, oils, perfumes, resins, dyes, gums, and alkaloids. When mixed with ethyl alcohol, ethyl ether becomes an excellent solvent for cellulose nitrate in the manufacture of guncotton, collodion solutions and pyroxylene plastics. It is used as a general anesthetic in surgery.

Dioxane - Dioxane is employed as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, resins, oils, waxes, oil and spirit-soluble dyes and many other organic as well as for some inorganic compounds.

Ethyleneglycol Monomethyl Ether - This material is used as a solvent for low viscosity cellulose acetate, natural resins, some synthetic resins and some alcohol-soluble dyes. It is also used in dyeing leather, sealing moisture proof cellophane, quick-drying varnishes and enamel nail polish, and in wood stains.

Ethyleneglycol Monoethyl Ether - This ether-alcohol is used to prepare bis(β-halo) derivatives of ethyleneglycol monoethyl ether and as a solvent for nitrocellulose, lacquers and dopes in varnish remover, cleaning solutions, dye baths, and in leather finishing.

Isopropyl Ether - This material may be converted to the alcohol or used as motor fuel additive. It is also used as a solvent in certain extraction processes and as a solvent in the manufacture of pharmaceuticals, smokeless powder, paint and varnish removers, and rubber cements.

Polypropylene Glycol Methyl Ether - This material is used as a component in lubricants.

Propylene Oxide - This epoxide is used in the manufacture of alkanolamines, polypropylene glycols, propylene glycol and in paint removers.

Tetrahydrofuran - This cyclic ether is used as a plasticizer, in paint removers, and as a solvent for high polymers. It is also employed in the synthesis of butyrolactone, succinic acid, and 1,4-butanediol diacetate.

Physical and Chemical Properties

The physical and chemical properties of these ethers are included in the attached worksheets.

2. TOXICOLOGY

The principal hazard in industrial use and handling of the ethers is from inhalation of their vapors. As a class, they do not penetrate the skin in harmful amounts nor are they irritating to the skin.[2401] The simpler ethers such as ethyl ether, isopropyl ether, etc., are powerful narcotics which in large doses can cause death.

3. OTHER HAZARDS

The more volatile ethers, such as ethyl and methyl ether, are particularly dangerous fire hazards because of their low ignition and flash points. Peroxides, which form in ethers upon standing, pose the additional threat of detonation when an ether is heated after prolonged storage.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Stringent safety precautions must be taken to guard against health and fire hazards whenever ethers are handled. The area in which highly flammable ethers are stored or used should be posted with "No Smoking" or other appropriate warning signs. If leaks or spills occur, only properly protected personnel should remain in the area. Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers. All spills should be flushed away promptly with water.

Ordinarily, ethyl ether will start to oxidize soon after distillation. Storage time required for this induction period, the rate at which oxidation will proceed and the quantity of peroxides that will be produced, may vary widely and will depend upon condtions that are not entirely understood. Ether peroxides are not as volatile as the corresponding ether and tend to concentrate during evaporation or distillation. Ether peroxides, when concentrated, may detonate with extreme violence.

Ether which is to be used in any process that will involve evaporation or distillation, must pass a standard test. Ethers failing the test must be treated to remove the peroxides.[2402]

Drums and other portable containers of ethyl ether should be stored out of the direct rays of the sun and away from sources of heat. These precautions are applicable to all of the lower, more volatile ethers.

A list of hazardous materials with packing and shipping instructions is found in Code of Federal Regulations,[0278] title 49, parts 100 to 199, and shipping instructions for ethyl ether are found in the Manufacturing Chemists Association bulletin SD-29.[2402]

Disposal/Reuse

Contaminated or degraded materials found to be unusable in a recycling process must be disposed of in a safe manner, defined in terms of the recommended provisional limits of the subject compounds in the environment. The recommended provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Diethyl ether	4 ppm (12 mg/M^3)	0.01 TLV
Dioxane	1.0 ppm (3.6 mg/M^3)	0.01 TLV
Ethylene glycol monoethyl ether	2.0 mg/M^3	Based on similar compounds
Ethylene glycol monoethyl ether acetate	0.25 ppm (1.2 mg/M^3)	Based on similar compounds
Isopropyl ether	2.5 ppm (10.5 mg/M^3)	0.01 TLV
Polypropylene glycol methyl ether	2.0 mg/M^3	Based on similar compounds
Propylene oxide	1.0 ppm (2.4 mg/M^3)	0.01 TLV
Tetrahydrofuran	2.0 ppm (5.9 mg/M^3)	0.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Diethyl ether	60 ppm (mg/l)	Stokinger and Woodward Method
Dioxane	18 ppm (mg/l)	Stokinger and Woodward Method
Ethylene glycol monoethyl ether	10 ppm (mg/l)	Based on similar compounds
Ethylene glycol monoethyl ether acetate	6.0 ppm (mg/l)	Based on similar compounds
Isopropyl ether	52.5 ppm (mg/l)	Stokinger and Woodward Method
Polypropylene glycol methyl ether	10 ppm (mg/l)	Based on similar compounds
Propylene oxide	12 ppm (mg/l)	Stokinger and Woodward Method
Tetrahydrofuran	29.5 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Recycling of Concentrated Waste

It would be advisable in all cases to first contact the manufacturer to determine if the material can be recycled. The applicability of this option depends on the type and extent of contamination or degradation the material has suffered.

Option No. 2 - Disposal of Concentrated Waste Containing No Peroxides[2402]

Prime factors to consider in the disposal of ethers are: possible presence of peroxides in liquid or on container elements; flash points; vapor density with respect to air; liquid flammability; explosive limits with air; and propensity to accumulate static electrical charges that may ignite vapors.

Waste materials containing lower molecular weight ethers should not be emptied into drains or sewers, as sewer explosions are likely to result. The vapors will travel long distances before dissipation, and a steam or process line may be hot enough to effect ignition.

Where there is certainty that peroxides are not present, disposal may be accomplished by discharging liquid (not vapor) at a controlled rate near a pilot flame. An inert gas line connected to the vapor phase and a valve controlled line from the bottom of the container will permit a gravity feed of the liquid to a pilot flame at a safe distance. The inert gas avoids contact of the liquid with air and will inert the vapor space in the container. The rate of burning can be valve controlled. Lines and containers should be grounded.

Option No. 3 - Disposal of Concentrated Waste Suspected of Containing Peroxides[2402]

Where peroxides are known to exist, or it is suspected that they might exist, it is suggested that no attempt be made to open the containers. (Peroxides tend to form in the threads of bungs and caps, and are easily ignited by the frictional heat generated when these closures are turned). Handling of the containers should be minimized. The containers should be destroyed from an upwind position of 100 feet or more away, using rifle fire so aimed that most of the ether will be forced to spill on the ground and evaporate. This should be done at a remote location, away from habitation, where no harm to the public or surroundings can occur. It should be remembered that there is always the possibility that fire may ensue or the container might explode. Alternatively, a blasting cap or small explosive charge may be used to perforate the container from a safe distance.

Option No. 4 - Incineration of Dilute Organic Wastes

Dilute organic waste can be safely incinerated provided the burning temperature is sufficiently high to reduce the waste to CO_2 and water.

Option No. 5 - Incineration of Dilute Aqueous Waste

Since ethers generally resist biological degradation,[0314] dilute aqueous waste containing ethers above preliminary limits for water and soil can be disposed of by incineration. It is recommended that dilute aqueous waste be thermally oxidized by spraying the aqueous solution into an incinerator which is at a temperature of at least 1500 F.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Most of the wastes generated by the industries that produce and use these materials can best be handled and treated at the site of the generation by methods discussed in Section 5. Since adequate methods are available for disposal of these materials and they can be implemented by the manufacturers and users, they are not judged to be candidate waste stream constituents requiring National Disposal Site treatment.

7. REFERENCES

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1571. Schnell Publishing Company, Inc. 1971-72 POD chemical buyers directory. 59th ed. New York, 1971. 1,584 p.

2401. Ethers. Bulletin F-40524. Union Carbide Chemical Company, New York. 41 p.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Diethyl ether (152)

IUC Name

Common Names Diethyl Ether
Sulfuric ether; anesthesic ether

Structural Formula

$C_2H_5OC_2H_5$

Molecular Wt. 74.12(1)   Melting Pt. -116.2 C(1)   Boiling Pt. 34.6 C(1)

Density (Condensed) 0.7135 @ 20/4 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

442 mm @ 20 C(1)   760 mm @ 34.6 C(1)   @

Flash Point -40 F(1)   Autoignition Temp. 356 F(1)

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (3)

Cold Water Soluble   Hot Water   Ethanol Soluble in all proportions

Others: Benzene, chloroform, oils, ligroin

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Sources(3): Allied Chemical Corp; Amsco Division; Ashland Chemical Co; Corco Chemical Corp; Mallinckrodt Chemical Works; McKesson Chemical Co; Mutchler Chemical Co; Publicker Industries Inc; Thompson-Hayward Chemical Co.

References (1) 0766
(2) 1570
(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ethylene glycol Monoethyl Ether (187)

IUC Name 2-methoxyethanol(1)

Common Names

Structural Formula

$CH_3OCH_2CH_2OH$

Molecular Wt. 76.11(1)   Melting Pt. -85.1(1)   Boiling Pt. 125(1)

Density (Condensed) 0.9647(1) @ 204 4 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (1)

Cold Water Infinite   Hot Water   Ethanol Very soluble

Others: Ether, benzene

Acid, Base Properties Neutral

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Sources(2): Eastman Chemical Products. Celanese Chemical Co; Union Carbide Corporation.

References (1) 1570

(2) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ethyleneglycol monoethyl ether acetate (188)

IUC Name

Common Names Ethylene Glycol Monoethyl-Ether Acetate ("Cellusolve" Acetate)

Structural Formula

$CH_3COOCH_2CH_2OC_2H_5$

Molecular Wt. 132.17(1)

Melting Pt. -61.7 C(1)

Boiling Pt. 156.4 C(1)

Density (Condensed) 0.9748 @ 20/20 C(1)

Density (gas) 4.72(1) air = 1.00 @

Vapor Pressure (recommended 55 C and 20 C)

1.2 mm @ 20 C(1)   @   @

Flash Point 120 F(1)

Autoignition Temp. 715 F(1)

Flammability Limits in Air (wt %) Lower   Upper

Explosive Limits in Air (wt. %) Lower 1.71 percent L.E.L Upper

Solubility(3)

Cold Water   Hot Water   Ethanol Soluble

Others: Ether, acetone

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Sources(2): A.I.D. Chemical Co; Amsco Division; Ashland Chemical Co; CPS Chemical Co; Celanese Chemical Co; Eastman Chemical Products; Stoney-Mueller Inc; Thompson-Hayward Chemical Co; Union Carbide Co.

References (1) 0766
(2) 1571
(3) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Isopropyl Ether (232)

IUC Name

Common Names Isopropyl ether
2-Isopropoxypropane

Structural Formula

$(CH_3)_2CHOCH(CH_3)_2$

Molecular Wt. 102.17$^{(1)}$ Melting Pt. -60 C$^{(1)}$ Boiling Pt. 68.5 C$^{(1)}$

Density (Condensed) 0.719 @ 25 C$^{(1)}$ Density (gas) 3.52$^{(1)}$ air = 1.00 @

Vapor Pressure (recommended 55 C and 20 C)

150 mm @ 25 C$^{(1)}$ 400 mm @ 48.2 C$^{(2)}$ @

Flash Point -18 F$^{(1)}$ Autoignition Temp. 830 F$^{(1)}$

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 1.4 percent Upper 21.0 percent

Solubility$^{(2)}$

Cold Water Slightly soluble Hot Water Ethanol Soluble in all proportions

Others: Ether

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Sources$^{(3)}$: A.I.D. Chemical Co; Allied Chemical Corp; Amsco Division; Publicker Industries; F. H. Ross & Co; Ruger Chemical Co; Shell Chemical Co; Stoney-Mueller Inc; Suburban Chemical Co; Thompson-Hayward Chemical Co; Union Carbide Corp.

References (1) 0766
(2) 1570
(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Propylene oxide (362)

IUC Name

Common Names Propylene Oxide
1,2-Epoxypropane, Propene oxide

Structural Formula

OCH_2CHCH_3

Molecular Wt. 58.08(1) Melting Pt. -104.4 C(1) Boiling Pt. 33.9 C(1)

Density (Condensed) 0.8304 @ 20/20 C(1) Density (gas) 2.0(1) @
air = 1.00

Vapor Pressure (recommended 55 C and 20 C)

400 mm @ 17.8 C(1) 760 mm @ 33.9 C(1) @

Flash Point -35 F(1) Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (vol %) Lower 2.1% Upper 21.5%

Solubility(2)

Cold Water Soluble in 100 parts Hot Water Ethanol Soluble

Others: Ether

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Sources(3): BASF Wyandotte Cor; Dow-Chemical Co; Jefferson Chemical Co; Olin Chemicals; Oxirane Corp; Union Carbide Corp.

References (1) 0766
(2) 1492
(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tetrahydrofuran (426)

IUC Name

Common Names Tetrahydrofuran
Cyclotetramethylene

Structural Formula

$OCH_2CH_2CH_2CH_2$

Molecular Wt. 72.10(1)
Melting Pt. -108.5 C(1)
Boiling Pt. 65.4 C(1)

Density (Condensed) 0.888 @ 20/4 C(1)
Density (gas) 2.5(1) @
air = 1.00

Vapor Pressure (recommended 55 C and 20 C)

114 mm @ 15 C(1)
@
@

Flash Point 1 F(1)
Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper
Explosive Limits in Air (wt. %) Lower Upper

Solubility(3)

Cold Water Soluble
Hot Water
Ethanol Soluble
Others: Ketones, ethers, hydrocarbons

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification
Coast Guard Classification

Comments Sources(3): Ashland Chemical Co; Conray Products Co; E. I. duPont de Nemours & Co; International Chemical Corp; McKesson Chemical Co; Pyramid Chemical Sales Co; Quaker Oats Co; Western Eaton Solvents & Chemicals Co.

References (1) 0766
(2) 1492
(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dioxane (153)

IUC Name

Common Names Diethylene dioxide
Dioxane

Structural Formula

$OCH_2CH_2OCH_2CH_2$

Molecular Wt. 88.10(1)
Melting Pt. 10 C(1)
Boiling Pt. 101.1 C(1)

Density (Condensed) 1.0353 @ 20/4 C
Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

40 mm @ 25.2 C(1)
100 mm @ 45.1 C(2)
@

Flash Point 54 F(1)
Autoignition Temp. 356 F(1)

Flammability Limits in Air (wt %) Lower Upper
Explosive Limits in Air (wt. %) Lower 1.97 percent Upper 22.2 percent(1)

Solubility(2)

Cold Water Soluble in all proportions
Ethanol Soluble in all proportions

Others: Ether, acetone, organic solvents, acetic acid

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification
Coast Guard Classification

Comments Mfg.(3): Amsco Division; Ashland Chemical Co; J. T. Baker Chemical Co; Corco Chemical Co; Grant Chemicals, Inc; MC&B Manufacturing Chemists; Southland Solvents and Chemical Co; Stoney-Mueller, Inc; Union Carbide Corp.

References (1) 0766
(2) 1570
(3) 1571

PROFILE REPORT

Dinitrobenzene (163)

1. GENERAL

Dinitrobenzenes range from white to yellowish crystals and are described as being highly toxic.[0766] They comprise three possible position isomers: 1,2-(mp, 118 C), 1,3-(mp, 89 C) and 1,4-(mp, 173 C).[1492]

The 1,3-isomer is prepared by the direct nitration of benzene using nitric acid and sulfuric acid.[1656] The material produced on a commercial basis generally consists of a mixture of isomers containing 91 to 94 percent of the meta compound.[1433] Oxidation of primary aromatic amines is the method used to prepare 1,2- and 1,4-dinitrobenzene since these compounds cannot be obtained in good yield by direct nitration.[1655] Meta-dinitrobenzene has been used as a substitute for TNT and other high explosives but because of its toxicity and the availability of more powerful explosives, it no longer is utilized in this way.[1433]

Meta-dinitrobenzene is produced commercially by E. I. duPont de Nemours and Company.[1571] It is considered unsuitable for handling on a mass-production basis because of its hazardous nature.[1433]

Physical/chemical properties of the three isomers are summarized in the attached worksheets.

2. TOXICOLOGY

Dinitrobenzene is described as being extremely toxic. It has an irritating effect on the respiratory system and causes the skin to become bluish in color.

3. OTHER HAZARDS

The dinitrobenzenes are considered to be severe explosion hazards.[0766,1433] When these materials are heated to decomposition, they emit highly toxic fumes of oxides of nitrogen and explode.[0766] All of the dinitrobenzenes should be treated as highly toxic materials and the skin, eyes and lungs should be protected accordingly.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

In handling dinitrobenzene, direct skin contact must be prevented by use of suitable protective clothing. These materials are to be protected from shock and heat to prevent fire and/or explosion.[0766]

Pertinent shipping regulations may be found in the Code of Federal Regulations, Title 49, Transportation, Sections 73.364, 73.371, 73.345 and 73.346 under the headings of dinitrobenzol, solid and dinitrobenzol, liquid. Under these regulations, dinitrobenzenes are classed as Poison B.

Disposal/Reuse

Disposal or reuse of waste dinitrobenzene streams must take into account the explosive and toxic nature of these materials. It is assumed that dilute aqueous waste streams containing dinitrobenzene are treated in the same manner as the dinitrophenol waste streams, i.e., secondary treatment using acclimated activated sludges and aeration (see Profile Report on dinitrophenol [164]).

Recommended provisional limits for dinitrobenze in the environment are as follows:

Contaminant and Environment	Provisional Limit	Basis of Recommendation
Dinitrobenzene in air	0.01 mg/M^3	0.01 TLV
Dinitrobenzene in water and soil	0.05 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dinitrobenzenes are expected to appear primarily as aqueous waste streams in low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Dinitrobenzenes

In the event it becomes necessary to dispose of a significant quantity of concentrated dinitrobenzene, incineration appears to be the only acceptable technique currently available. Qualified personnel familiar with handling toxic and explosive materials must be available to operate the facility. The dinitrobenzene must be diluted with other combustible materials which are not explosive and incinerated under controlled conditions where oxides of nitrogen are removed from the effluent gas by scrubbers, and/or catalytic or thermal devices.[1435] Combustion should be carried out at a minimum temperature of 1,800 F over a minimum residence time of 2.0 seconds.

Dilute Aqueous Waste

Dinitrobenzene appears as aqueous waste in the manufacturing process. Other sources of waste are from water used in the cleaning of equipment used in dinitrobenzene service. It is assumed that methods used to dispose of aqueous dinitrobenzene waste are similar to methods for dinitrophenol, i.e., secondary treatment utilizing activated sludges. The adequacy of this practice is in doubt due to the apparent difficulty of microorganisms to degrade aromatic nitro compounds.[1044] Until data are available to show that dinitrobenzenes can be degraded satisfactorily in secondary treatment facilities, it is recommended that aqueous waste streams be concentrated and treated as discussed in the section on concentrated dinitrobenzenes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The dinitrobenzenes do not appear to be candidate waste stream constituents for National Disposal Sites since they may be treated by common industrial techniques. It is anticipated that the great majority of the aqueous dinitrobenzene waste generated in the chemical industries will continue to be treated at the source of the waste generation, and/or industrial disposal facilities but that emphasis should be changed from biological treatment processes to concentration and subsequent controlled incineration until the efficiency of the biological processes is proven. In the event concentrated material becomes contaminated, it can be incinerated as discussed in the section on Concentrated Dinitrobenzenes.

7. REFERENCES

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1656. Condon, F. E., and H. Meislich. Introduction to organic chemistry. New York, Holt, Reinhart, and Winston, Inc. 1956. 841 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrobenzene (163)

IUC Name 1,2-dinitrobenzene

Common Names O-dinitrobenzol, ortho-dinitrobenzene

Structural Formula

$C_6H_4(NO_2)_2$

Molecular Wt. 168.11 Melting Pt. 118 C Boiling Pt. 302.8 C @ 770 mm.

Density (Condensed) 1.571 @ 0C/4C Density (gas) 5.79 (air=1) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point 302 F Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Slightly Soluble(2) Hot Water Ethanol Soluble(2)

Others: Very soluble in chloroform(2) hot alcohol(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Volatile with steam(3)

References (1) (0766)

(2) (1570)

(3) (1492)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrobenzene (163)

IUC Name 1,4-dinitrobenzene

Common Names 1,4-dinitrobenzene, para-dinitrobenzol

Structural Formula

$C_6H_4(NO_2)_2$

Molecular Wt.(1) 168.11 Melting Pt.(1) 172 C Boiling Pt. 299C @ 777 mm

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility.

Cold Water Insoluble(1) Hot Water Ethanol Slightly Soluble(1)

Others: Soluble in chloroform(1) acetic acid(1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Volatile with steam. LD orally in cats: 29.4mg/kg(2)

References (1) (1570)
(2) (1492)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrobenzene (163)

IUC Name 1,3-dinitrobenzene

Common Names m-dinitrobenzol, meta-dinitrobenzene

Structural Formula

$C_6H_4(NO_2)_2$

Molecular Wt.(1) 168.11   Melting Pt.(1) 90 C   Boiling Pt.(1) 291 C @ 756 mm.

Density (Condensed) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water Insoluble(1)   Hot Water   Ethanol Very Sol hot(1)

Others: Soluble in ether(1), chloroform(1) very soluble in benzene(1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Volatile with steam.(2)

References (1) (1570)
(2) (1492)

PROFILE REPORT

Dinitrophenol (164)

1. GENERAL

The dinitrophenols are yellowish crystals described as being highly toxic[0766] and readily adsorbed through the intact skin.[1492] They comprise six possible position isomers:[1492,0766,1570] 2,3-(mp, 144 C); 2,4-(mp, 112 C); 2,5-(mp, 108 C); 2,6-(mp, 63 C); 3,4-(mp, 134 C); 3,5-(mp, 126 C).

Partially or fully nitrated phenols are obtained in industry by hydrolyzing the corresponding chloro compounds with dilute alkali. The dinitrophenols are then reduced to yield amino phenols which are employed as intermediates for dyes, pharmaceuticals, and photographic chemicals.[1433]

Large scale commercial facilities for the manufacture of dinitrophenol are operated by American Aniline Products, American Hoechst Corporation and Southern Dyestuff Company.[1571] Physical/chemical properties are summarized in the attached worksheets.

2. TOXICOLOGY

Dinitrophenol is a moderate to severe health hazard for both acute and chronic exposures. Liver and kidney damage have been reported in chronic poisoning.[1564] Fatal cases have been reported in the literature from the inhalation of the dust in a concentration estimated to be 40 mg/M^3.[0766] Dinitrophenol is readily absorbed through intact skin and its vapors are absorbed through the respiratory tract.[1492]

Based upon comparable data and experience for dinitro-o-cresol, it is believed that a level of 0.2 mg/M^3 for an exposure time of eight hours is safe.[1564] Care should be exercised in handling to prevent contact of the material with the skin, eyes, or clothing.

3. OTHER HAZARDS

The 2,3-dinitrophenol is considered to be a severe explosion hazard. The 2,4- and 2,6-isomers are only moderately hazardous in this respect.[0766] Information on 2,5-, 3,4- and 3,5- is not available but should be assumed to represent a potential hazard. All the dinitrophenols should be treated as moderate to highly toxic materials and the skin, eyes and lungs should be protected accordingly.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The recommended control procedure[1564] for dinitrophenols requires that direct skin contact be prevented by use of suitable protective clothing. Where exhaust ventilation cannot effectively control dust and mist exposures, respirators should be provided. Strict personal cleanliness and frequent change of clothing is advised. Safety showers and eye wash fountains should be provided in areas where these materials are handled.

Pertinent shipping regulations may be found in the Code of Federal Regulations, Title 49, Transportation, Sections 73.345 and 73.362a. Under these regulations, dinitrophenol solutions are classed as Poison B.

Disposal/Reuse

Southern Dyestuff Company[1450] is currently under partial sponsorship by the EPA to conduct studies pertaining to experimental treatment processes for aqueous dinitrophenol waste streams. The main effort of the research is directed toward the development of secondary disposal techniques to handle dilute waste water streams containing 2,4-dinitrophenol. The Hyperion Plant in El Segundo, California[1621] will accept dinitrophenol only under controlled conditions and at very low volumes.

Recommended provisional limits of dinitrophenol in the environment are as follows:

Contaminant and Environment	Maximum Concentration and Point Source Release Rate	Basis for Recommendation
Dinitrophenol in Air	0.002 mg/M^3	0.01 TLV
Dinitrophenol in Water and Soil	0.010 ppm(mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dinitrophenol is expected to appear primarily in aqueous waste streams at low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Dinitrophenol

In the event it becomes necessary to dispose of a significant quantity of concentrated dinitrophenol, three disposal options are available. These options are:

Option No. 1 - Recycle. The first option is to contact the manufacturer and determine if it is possible to return the material. Southern Dyestuff Company[1450] has indicated a willingness to accept concentrated dinitrophenol for reprocessing. The option of recycling the material is adequate and should be used whenever possible.

Option No. 2 - Incineration. Incineration is the second choice option provided controlled combustion processes where the oxides of nitrogen are scrubbed from the effluent gas are used or where a thermal device[1435] is used to reduce the oxides of nitrogen to their elemental form. The material should be combusted at a minimum temperature of 1,800 F for at least 2.0 seconds.

Option No. 3 - Sanitary Landfill. Sanitary landfills are generally not recommended because of the potential of ground and surface water pollution as well as possible occupational hazards resulting from on-site handling.[0620] However, California Class I-type landfills are adequate when the material is contained and has low vapor pressure.

Dilute Aqueous Waste

Dinitrophenol appears in the aqueous waste streams manufacturing process. Other sources of waste are water used in the cleaning of equipment used in dinitrophenol service. Methods for adequately handling the disposal of dilute aqueous solutions of dinitrophenol are currently under study by the Southern Dyestuff Company under the partial sponsorship of EPA[1450] since effectiveness of the present secondary treatment techniques utilizing activated sludges to dispose of dilute aqueous waste are in question.

Dinitrophenol can, under controlled conditions, be discharged into a municipal sewage system at very small volumes,[1621] but the adequacy of this practice is in doubt due to the apparent difficulty of microorganisms to degrade aromatic nitro compounds.[1044] Until data are available to show that dinitrophenol can be degraded satisfactorily in secondary treatment facilities, it is recommended that aqueous waste streams be concentrated and treated as discussed in the section on concentrated dinitrophenol.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The dinitrophenols do not appear to be candidate waste stream constituents for National Disposal Sites. It is anticipated that systems to handle the great majority of the aqueous dinitrophenol waste generated in the chemical process industries will continue to be located at the source of the waste generation, but that empahsis should be changed from biological treatment processes to concentration and subsequent controlled incineration until the adequacy of the biological processes is proven. In the event concentrated material becomes contaminated, manufacturers of dinitrophenol can be contacted and arrangements made to return the material for recycling, or, if need be, it can be incinerated as discussed in the section on Concentrated Dinitrophenol.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 2,3-dinitrophenol

Common Names 2,3-dinitrophenol
1-hydroxy-2,3-dinitrobenzene

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1) Melting Pt. 144 C(1) Boiling Pt. ______

Density (Solid) 1.681(1) @ 20 C Density (gas) 6.35(1) @ ______ ______
Air = 1

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility (2)

Cold Water Slightly soluble Hot Water ______ Ethanol Very soluble in hot ethanol

Others: ether (very soluble)

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification ______ Coast Guard Classification ______

Comments Sources(3) Not listed

References (1) 0766
(2) 1570
(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 2,4-dinitrophenol

Common Names 2,4-dinitrophenol

LD_{50} orally rats 30 mg/kg(4)

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1) Melting Pt. 112 C(1) Boiling Pt. _____

Density (Solid) 1.683 @ 24 C(1) Density (gas) 6.35(1) @ _____ _____

Air = 1

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____ _____ @ _____ _____ @ _____

Flash Point _____ Autoignition Temp. _____

Flammability Limits in Air (wt %) Lower _____ Upper _____

Explosive Limits in Air (wt. %) Lower _____ Upper _____

Solubility(2)

Cold Water Slightly soluble Hot Water _____ Ethanol _____

Others: ether, benzene, chloroform

Acid, Base Properties _____

Highly Reactive with _____

Compatible with _____

Shipped in _____

ICC Classification _____ Coast Guard Classification _____

Comments Sources(3): American Aniline Products, Inc.; Southern Dyestuff Company

References (1) 0766
(2) 1570
(3) 1571
(4) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 2,5-dinitrophenol

Common Names 2,5-dinitrophenol

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1) Melting Pt. 108 C(1) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility(1)

Cold Water Slightly soluble Hot Water Ethanol Slightly soluble

Others: Soluble in hot alcohol, ether, fixed alkali hydroxide

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 2,6-dinitrophenol

Common Names 2,6-dinitrophenol

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1) Melting Pt. 63 C Boiling Pt.

Density (Condensed) @ Density (gas) 6.35(1) @

Air = 1

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Slightly soluble(4) Hot Water Soluble(2) Ethanol Very soluble in hot ethanol(2)

Others: ether (very); benzene, chloroform

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Sources:(3) American Hoechst Corp., Organic Intermediate Dept.

References (1) 0766

(2) 1570

(3) 1571

(4) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 3,4-dinitrophenol(1)

Common Names 3,4-dinitrophenol

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1)   Melting Pt. 134 C(1)   Boiling Pt.

Density (Condensed) 1.672(1) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (1)

Cold Water Slightly soluble   Hot Water   Ethanol Soluble

Others: Soluble in ether

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitrophenol (164)

IUC Name 3,5-dinitrophenol(1)

Common Names 3,5-dinitrophenol

Structural Formula

$(NO_2)_2C_6H_3OH$

Molecular Wt. 184.11(1) Melting Pt. 126.1 C(1) Boiling Pt.

Density (Condensed) 1.702(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol Soluble(1)

Others: Soluble in benzene, chloroform, slightly soluble in ligroin

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570

PROFILE REPORT

Diphenylamine (167)

1. GENERAL

Diphenylamine is a white crystalline substance described as being highly toxic.[0766] The commercial product is sold as very pale tan flakes, light tan fused solid, and amber to brown liquid.[1669]

Diphenylamine is produced by heating aniline with aniline hydrochloride at 210 to 240 C at a pressure of 90 psi. If a catalyst is used, aniline will form diphenylamine in the absence of the hydrochloride. Diphenylamine is widely used as a rubber antioxidant, as an intermediate for pharmaceuticals, and when fused with sulfur as an insecticide. It has also been used as a stabilizer for explosives and in the preparation of azo dyes.[1433]

Commercial facilities for the manufacture of diphenylamine are operated by American Cyanamid Co. and E. I. duPont de Nemours and Company, Inc.[1571]

The physical/chemical properties of diphenylamine are summarized in the attached worksheet.

2. TOXICOLOGY

Diphenylamine is highly toxic when ingested, inhaled, or absorbed through the skin.[0766] The Threshold Limit Value (TLV) of 10mg/M^3 is based on industrial experience and is known to be sufficiently low to prevent systemic poisoning. Although the vapor pressure is low[0766], diphenylamine may be irritating to mucous membranes [1492], if inhaled as the the dust or vapor. Animal experiments indicate that it is poorly absorbed through the skin.[1669] Symptoms of diphenylamine poisoning include bladder trouble, tachycardia, hypertension and skin trouble.

Protective clothing, safety glasses, and respirators (if dust exposure is possible) should be used when handling diphenylamine. The decomposition products evolved upon heating dephenylamine are highly toxic.[0766]

3. OTHER HAZARDS

Diphenylamine should be kept away from open flames, sparks and heat.[1669] Although it emits highly toxic fumes when heated to decomposition,[0766] it is only considered a slight fire hazard. Diphenylamine is not considered hazardous to health under normal conditions of industrial use.[1669]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Although experiments[1699] indicate that diphenylamine is not readily absorbed through the skin, direct skin contact should be prevented by use of suitable protective clothing. Where exhaust ventilation cannot effectively control dust and mist exposures, respirators should be provided.

Bulk diphenylamine may be stored in steel equipment for extended periods of time provided that the temperature is maintained below 65 C. Prolonged storage at temperatures above 65 C will accelerate discoloration of the product.[1669]

Diphenylamine is shipped in polyethylene lined paper bags, and 8,000 and 10,000 gallon tank cars. Shipping classification for diphenylamine is chemical-NOI-no labels required.[1669]

Disposal/Reuse

Diphenyl is found as dilute waste in the tars which appear as bottom products in the manufacturing processes. Aqueous waste streams are not associated with the manufacture of diphenylamine. Criteria for disposing of organic diphenylamine waste streams must take into account the toxicity of the material, and byproducts of disposal. Recommended provisional limits for diphenylamine in the environment are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Diphenylamine	0.1 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Diphenylamine	0.5 ppm(mg/l)	Stokinger & Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Diphenylamine is expected to appear primarily in organic waste streams at low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Diphenylamine

In the event it becomes necessary to dispose of a significant quantity of concentrated diphenylamine wastes, and purification/recycling is impractical, then incineration of the diphenylamine is the recommended method of disposal. The material must be incinerated under controlled conditions where oxides of nitrogen are removed from the effluent gas by scrubbers and/or thermal or catalytic devices.[1435] Land burial of concentrated diphenylamine wastes is a satisfactory means of disposal provided the site is acceptable from a geologic and ground water hydrology standpoint and meets California Class 1-type landfill standards.

Dilute Organic Waste Streams

Diphenylamine appears as dilute waste in the tars which appear as bottoms products in the manufacturing processes. Currently, these tars are disposed of in a plant landfill.[1520] Disposal of dilute waste in plant landfills is a satisfactory means of disposal provided the site is acceptable from a geologic and ground water hydrology standpoint and meets California Class 1 landfill requirements. Incineration is also an adequate method of disposal.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Diphenylamine is not judged to be a candidate waste stream constituent requiring National Disposal Site treatment since the various waste forms containing this material can be treated at the site of generation with the common industrial and municipal techniques discussed in Section 5.

7. REFERENCES

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1656. Condon, F. E., and H. Meislich. Introduction to organic chemistry. New York, Holt, Rinehart and Winston Inc. 1960. 841 p.

1669. American Cyanamid Company. Diphenylamine. Bound Brook, New Jersey 1969. 1 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET #167

H. M. Name Diphenylamine (167)

IUC Name

Structural Formula

$(C_6H_5)_2$ NH

Common Names Diphenylamine
Phenylaniline

Molecular Wt. 169.24 (1) Melting Pt. 52.9 C (1) Boiling Pt. 302 C (1)

Density (Condensed) 1.16 (1) @ Density (gas) 5.82 (1) (Air=1) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 108.3 C (1) @ @

Flash Point 307 F (1) (cc) Autoignition Temp. 846 F (1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble (5) Hot Water Ethanol Soluble (5)

Others: Freely soluble in propyl alcohol, benzene, ether, glacial acetic acid, carbon disulfide (5)

Acid, Base Properties Appx neutral (3)

Highly Reactive with Hexachloromelamine, trichloromelamine (4)
Forms salts with strong acids (5)

Compatible with mild steel (6)

Shipped in polyethylene lined paper bags, tank cars (6)

ICC Classification Coast Guard Classification

Comments Mfg (7) American Cyanamid Co., E. I. duPont de Nemours and Co. Inc.

References (1) (0766) (4) (1569) (7) (1571)
(2) (1656) (5) (1492)
(3) (1433) (6) (1669)

PROFILE REPORT ON
HALOGENATED ALIPHATIC HYDROCARBON FUMIGANTS
Ethylene Bromide (182), Methyl Bromide (267), Methyl Chloride (268)

1. GENERAL

Introduction

Fumigants are chemicals which are distributed through space as gases, and therefore, at a given temperature and pressure must exist in the gaseous state in sufficient concentration to be lethal to the insect pest. This physical requirement greatly limits the number of insecticides which may be used as fumigants, and most of the fumigants marketed today are halogenated hydrocarbons with high vapor pressures. Methyl bromide is one of the most widely used general fumigants, and ethylene bromide (ethylene dibromide) is an effective soil fumigant because of its slower release rate of vapors. Methyl chloride, though not used primarily as a fumigant, is often employed in aerosol bombs to control flying insects in enclosed premises.

The 1970 production figures for the three fumigants are: ethylene bromide, 296,826,000 lb; methyl bromide, 21,047,000 lb; and methyl chloride, 422,678,000 lb.[1718] All three commodities are expected to sustain a moderate-to-good growth rate in the near future despite the fact that ethylene bromide is also used as a component of antiknock fluid in conjunction with lead alkyls and the possible phasing out of leaded gasoline.[1506]

Manufacture

Ethylene Bromide. Ethylene bromide is manufactured by reacting ethylene and bromine in either batch or continuous processes, with the final product obtained by fractional distillation after washing the reactor effluent with dilute aqueous alkali to remove small quantities of hydrogen bromide.[1808] The U.S. producers of ethylene bromide include the following[1506,1966]:

Dow Chemical Company, Midland, Michigan.
Ethyl Corporation, Bromet, Arkansas.
Ethyl Corporation, Houston, Texas.
Great Lakes Chemical Corporation, El Dorado, Arkansas.
Houston Chemical Company, Beaumont, Texas.
Michigan Chemical Corporation, El Dorado, Arkansas.

Methyl Bromide. Methyl bromide is usually manufactured by using elementary bromine together with a reducing agent as the source of hydrogen bromide for reaction with methanol. The reducing agents that have been employed include sulfur dioxide, hydrogen sulfide, and sulfur raw oil, and both batch and continuous processes have been carried out industrially.[1808] The current U.S. producers of methyl bromide are [1506,1818]:

Dow Chemical Company, Midland, Michigan
Great Lakes Chemical Corporation, El Dorado, Arkansas.
Kerr-McGee Chemical Corporation, Los Angeles, California.
Michigan Chemical Corporation, St. Louis, Michigan.

Methyl Chloride. The two principal processes for industrial production of methyl chloride are chlorination of methane and reaction of hydrogen chloride with methanol. The methanol-hydrogen chloride reaction yields methyl chloride as the sole product, whereas chlorination of methane yields other chlorinated hydrocarbon coproducts of equal commercial importance in substantial amounts, such as methylene chloride and carbon tetrachloride. The U.S. producers of methyl chloride include the following[1506,1718]:

Allied Chemical Corporation, Moundsville, West Virginia.
Ancon Chemical Corporation, West Lake, Louisiana
Dow Chemical Company, Freeport, Texas.
Dow Chemical Company, Pittsburgh, California.
Dow Corning Corporation, Carrollton, Kentucky.
Dow Corning Corporation, Midland, Michigan.
E. I. Du Pont de Nemours & Company, Niagara Falls, New York.
Ethyl Corporation, Baton Rouge, Louisiana
Vulcan Materials Company, Chemical Division, Newark, New Jersey.
Union Carbide Corporation, Institute, West Virginia.

Uses

Ethylene bromide is used mostly as an ingredient of automobile and aircraft fuels to aid in removing lead from the engine cylinders. The next most important use is an active ingredient of grain fumigant formulations for insect control and of soil fumigants for the control of wireworms and nematodes. Other much smaller uses are as a nonflammable solvent for resins, gums, and waxes, and as an intermediate in synthesis.[1433]

The major use of methyl bromide is in the extermination of insect and rodent pests, as the compound is very suitable for the fumigation of food commodities and areas in which they are processed and stored, as well as for tobacco and nursery stock. Methyl bromide has also been used as a fire extinguisher, although its application is limited due to its high toxicity. In moderately small amounts, methyl bromide is used in organic synthesis, particularly as a methylating agent.[1433]

The principal uses of methyl chloride are in the manufacture of silicon butyl rubber, tetramethyl lead, and methyl cellulose. Methyl chloride is also used as a fumigant in controlling flies and other flying insects, but the application in this area amounts to a small proportion of its total usage. Other industrial applications include its use as a methylating agent in the production of quaternary ammonium compounds and of triptane, and as starting material in the manufacture of methylene chloride, chloroform, carbon tetrachloride, and of various bromochloro- and chlrofluoro-methanes.[1433]

Sources and Types of Wastes

The sources of ethylene bromide, methyl bromide, and methyl chloride wastes may include the following: (1) manufacturers of the chemicals; (2) pesticide formulators; (3) wholesalers of the chemicals; (4) professional applicators; (5) agricultural users; (6) government facilities that store, transport, and use the chemicals; (7) commercial and industrial processes utilizing these chemicals--gasoline formulation in the case of ethylene bromide and silicone, butyl rubber, tetramethyl lead and methyl cellulose manufacturers in the case of methyl chloride.

In general, ethylene bromide, methyl bromide, and methyl chloride wastes can be classified as either diluted or concentrated wastes. Diluted aqueous wastes include those generated in the waste waters of the manufacturers and formulators. Diluted gaseous wastes include gas streams in the manufacture of other products that require purification and removal of these toxic halohydrocarbons, and also any gas streams released to the atmosphere containing these compounds. Concentrated wastes normally include any unused or contaminated chemicals, and materials left in containers after emptying.

As fumigants, methyl bromide and ethylene dibromide have both been used alone or in combination with each other in various proportions. The most common methyl bromide formulation is as a liquified gas containing 2 percent chloropicrin stored in returnable pressurized containers.[1808] Ethylene bromide is frequently used mixed with carbon tetrachloride, carbon disulfide or ethylene dichloride,[1808] although it is sometimes formulated as emusifiable concentrates. Any surplus methyl bromide and ethylene bromide fumigants will probably be found in these common commercial formulations.

Physical and Chemical Properties

The physical and chemical properties of ethylene bromide, methyl bromide and methyl chloride are summarized in the attached worksheets.

2. TOXICOLOGY

Ethylene bromide is highly toxic to man and animals, and is readily absorbed through lungs, intact skins, and the gastrointestinal tract. Continued exposure to low doses causes irritation of the eyes, nose, respiratory tract, and finally paralysis of the hind legs from which the animal may recover eventually. Through errors in labeling, it has been used occasionally in place of ethyl bromide in anesthesia, leading to cases of fatal poisoning as a result of cardiac failure. Contact with the skin may cause injury with blister formation.[1808]

Methyl bromide is a highly toxic substance of insidious action. Single exposures to 1,000 ppm for 30 to 60 minutes are dangerous to life. The effects are on both respiratory and central nervous system, although death is usually caused by lung irritation resulting in congestion and edema. The early symptoms of fatal poisoning are headache, visual disturbances, nausea and vomiting, smarting of the eyes, irritation of the skin, listlessness, vertigo, and tremor. Exposure to concentrations as low as 100 to 500 ppm over a period of time may lead to chronic poisoning, resulting in a variety of symptoms and signs, most of which are due to injury of the central nervous system and include blurred or double vision, slurred speech, numbness of the extremities, mental confusion, hallucinations, tremor, coma, or frequent fainting attacks. Recovery is often prolonged and there may be permanent injury, such as sensory disturbances, weakness, disturbances of guilt,irritability, and blurred vision. In addition, liquid methyl bromide is an extreme irritant to the skin and may produce severe burns.[1301,1810]

Methyl chloride is a dangerous anesthetic and narcotic, about one-fourth as active as chloroform, and presents serious problems to life and health when inhaled in high concentrations. Poisoning by methyl chloride produces the following characteristic symptoms: drowsiness, mental confusion, coma, nausea, vomiting, and in severe cases, convulsions and death. It is dangerous in that after apparent recovery from seemingly mild exposures, serious and sometimes fatal return of symptoms may occur even after an interval of several days. It is absorbed quickly but eliminated rather slowly, and for this reason repeated exposures are hazardous. Recovery after what may appear to be a relatively slight exposure may be delayed 2 to 3 weeks, and after severe exposure some effects on the nervous system may be present for months or even years. Severe exposure may also effect the liver, kidneys, and blood forming tissues, lead to an increase in pulse rate, temperature, and breathing rate. Acute poisoning of methyl chloride is relatively rare, but might occur with exposures to well over 500 ppm. The type of poisoning occuring most frequently is due to repeated exposure to concentrations less than 500 ppm. Although methyl chloride is in its vapor state at ordinary temperatures and will produce little or no local effect, a stream of concentrated vapor striking the skin may result in a condition resembling frost bite followed by reddening, and occasionally, blister formation.[1301,1811]

The American Conference of Governmental Industrial Hygienists recommended Threshold Limit Values (TLV) for these compounds in air are: ethylene bromide, 20 ppm or 145 mg/M^3; methyl bromide, 15 ppm or 60 mg/M^3; and methyl chloride, 100 ppm or 210 mg/M^3.

Because of their volatility, the water pollution hazards arising from the human toxicity of methyl bromide and methyl chloride are relatively slight. For ethylene bromide, the approximate lethal dose to man has been estimated to be 65 mg/kg body weight.[1312]

No actual published data of aquatic toxicity for the three compounds were found. However, the National Research Council's Committee on Hazardous Materials, based on the physical properties of these compounds and their chemical similarity to other chemicals of known toxicity, has given a Grade 3 aquatic toxicity rating to ethylene bromide and a Grade 1 aquatic toxicity rating to methyl bromide and methyl chloride.[0311] Although a Grade 3 rating normally indicates a threshold range of 1 to 100 ppm to aquatic life and a Grade 1 rating a threshold range of 1,000 to 10,000 ppm to aquatic life, these ratings were also modified in some cases for chemicals having low water solubility or high volatility to account for the lower probability of water pollution, and this explains the low aquatic toxicity ratings given to methyl bromide and methyl chloride.

3. OTHER HAZARDS

Ethylene bromide is a nonflammable liquid, but reacts vigorously with metals such as aluminum, magnesium, sodium and potassium, strong alkalies, and oxidizing agents.[0096] An explosion may result if a mixture of liquid ammonia and ethylene bromide is allowed to warm up to room temperature.[1433]

At atmospheric pressure methyl bromide is practically nonflammable. Methyl bromide is also not particularly corrosive to most metals, although it attacks aluminum and magnesium and their alloys. With aluminum, methyl bromide forms the spontaneously ignitable aluminum trimethyl.[1810]

Methyl chloride is thermally stable, but may break down to produce hydrogen chloride and other toxic gases at high temperatures. It hydrolyzes slowly in water or upon contact with moisture, with the formation of hydrochloric acid, and is therefore corrosive. In addition, the hydrochloric acid formed attacks most metals with the evolution of hydrogen, which may form explosive mixtures with air. When dry, methyl chloride is inert towards most engineering materials except zinc, aluminum, magnesium, and their alloys. However, once reaction of methyl chloride with these metals or alloys initiates, it is greatly accelerated by the reaction products, resulting in rapidly increasing pressure if confined, and the release of gases which may ignite spontaneously.[1811]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Ethylene bromide, methyl bromide, and methyl chloride are all toxic by inhalation or skin contact. Full protective clothing and the use of a respirator are recommended in their handling and application. In cases of accidental contact, all contaminated clothing should be removed immediately and the skin washed thoroughly with soap and water.[0096,1810,1811]

Storage of these chemicals should be in cool, dry, well-ventilated areas, away from acute fire hazards. Because of their low boiling points, containers or storage vessels of methyl bromide and methyl chloride should also be protected from excessive heat and against sudden rise in temperatures.[1810,1811]

Methyl bromide is classified by the U.S. Department of Transportation (DOT) as a Poisonous Liquid, Class B, and methyl chloride is classified by DOT as a Flammable Compressed Gas. As such, both chemicals must be packed in DOT specification containers when shipped by rail, water, or highway and all DOT regulations governing loading, handling, shipping, and labeling must be complied with. Ethylene bromide is not classified by DOT, but due to its toxic nature, the same regulations governing the handling, loading, and shipping of Class B Poisonous Liquids should also be followed here.

Additional information on the safe handling and use of methyl bromide and methyl chloride are described in greater detail in the Chemical Safety Data Sheets SD-35 and SD-40 published by the Manufacturing Chemists Association.

Disposal/Reuse

Contaminated or degraded ethylene bromide, methyl bromide and methyl chloride are usually not considered for reprocessing, although manufacturers would normally accept these for disposal. For safe disposal of ethylene bromide, methyl bromide, or methyl chloride, the following provisional limits are recommended:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Ethylene bromide	1.45 mg/M^3	0.01 TLV
Methyl bromide	0.6 mg/M^3	"
Methyl chloride	2.1 mg/M^3	"

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Ethylene bromide	7.25 ppm (mg/l)	Stokinger and Woodward Method
Methyl bromide	3.0 ppm (mg/l)	Stokinger and Woodward Method
Methyl chloride	10.5 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Ethylene bromide, methyl bromide and methyl chloride generally do not present pollution problems to the chemical industry and very few specific efforts have been made to study their control or disposal. For these reasons, most of the removal, disposal, or recovery techniques discussed here are near future processes where no quantitative data are available.

Removal from Air

Option No. 1 - Refrigerated Condensation. When present in sufficiently high concentrations, refrigerated condensation has been used and is the recommended method for removing ethylene bromide, methyl bromide, or methyl chloride from air or a gas stream.[1965,1966,1972,1986] The halohydrocarbons are almost completely recovered, and the remaining traces can be removed by the other processes described here.

Option No. 2 - Monoethanolamine Scrubbing. Monoethanolamine (MEA) is commonly used for the removal of acid gases (hydrogen sulfide and carbon dioxide) in scrubbing towers. The absorption of ethylene bromide and methyl bromide by MEA has been used in the analytical determination of these compounds in air.[2029,2031] This indicates that MEA scrubbing could also be conceivably employed in removing these compounds from air on the commercial scale, although it remains to be demonstrated that the fouled MEA could be readily regenerated by methods such as steam stripping.

Option No. 3 - Alkaline Alkoxide Scrubbing. Ethylene bromide, methyl bromide, and methyl chloride could all be readily absorbed from the air by scrubbing with a solution of potassium or sodium hydroxide in anhydrous methanol and ethanol.[1301,2032] In the case of ethylene bromide, vinyl bromide is immediately formed, although further dehalogenation occurs very slowly in the alcoholic solution.[2030] For methyl bromide and methyl chloride, either the dimethyl ether or the methyl ethyl ether is formed, depending on whether methanol or ethanol is used in the absorbent. In fact, the reaction between alkyl halides and alkali alkoxides is the well-known Williamson ether synthesis and provides a method of preparing symmetrical and unsymmetrical ethers.[1808] The time required to reach 100 percent conversion of a known amount of methyl bromide in a potassium hydroxide-methanol solution at different temperatures has been measured and reported by Dumas and Latimer,[2032] and their results showed that complete conversion was obtained in 7 hr at 75 F or only 45 min at 157 F with 1N potassium hydroxide in methanol. However, similar experiments have not been conducted with either methyl chloride or ethylene bromide, and the effectiveness of alkali alkoxides as an absorbent for the alkyl halides on the commercial scale has yet to be proven.

Option No. 4 - Alcohol Scrubbing. Dow has experimented with the use of methanol scrubbing for the removal of methyl bromide from air, but to date only marginal results are obtained for the low methyl bromide concentration ranges (0.1%) investigated.[1969] When higher concentrations of methyl bromide in the air are encountered, however, Dow believes methanol scrubbing would be an effective means to achieve a high rate of removal. Ethylene bromide has also been reported to be readily absorbed from air by shaking with ethyl alcohol,[2030] but again,data are not available to determine the applicability of the process on commercial scale.

Option No. 5 - Adsorption with Activated Carbon. Activated carbon is extensively employed for the removal of traces of gas impurities from air and it has been suggested that small quantities of ethylene bromide, methyl bromide, or methyl chloride could be effectively removed from air by passage through activated-carbon traps or beds.[1986,1987]

Removal from Water

Ethylene bromide is only slightly soluble in water and most if it can be removed from water in a gravity separator or a settling pond due to its density which is more than twice that of the water.[1965,1967] Methyl bromide is practically insoluble in water and is also extremely volatile, and hence does not contribute to water pollution. Methyl chloride is slightly soluble in water but again is also very volatile and can be readily removed from water by simple physical methods. Some of the techniques used for treating water contaminated with these compounds are described below briefly.

Option No. 1 - Steam Stripping. Steam stripping is a widely used disposal method in the chemical and petrochemical industry and can be used to remove ethylene bromide, methyl bromide, or methyl chloride from water.[1970,1972,1987] The waste gases from stripping must be burned in incinerators equipped with adequate scrubbing to totally prevent air pollution.

Option No. 2 - Blowing with Air. The Manufacturing Chemists Association recommends removing methyl chloride from water by blowing the contaminated water with air, and burning the outlet air stream in cases of gross contamination, with a flash arrestor on the vent line.[1811] Air blowing can also be used in removing the equally volatile methyl bromide from water.

Option No. 3 - Adsorption with Activated Carbon. The engineering firm of Camp, Dresser, and McGee has completed a pilot scale investigation on the use of both powdered and granular activated carbon for the removal of chlorinated hydrocarbons from the combined waste waters of several chemical plants in the Niagara Falls, New York area, including the Du Pont facility there that manufactures methyl chloride.[1971,1992] Although the removal of any of the individual compounds was not separately studied, the pilot work was considered a success and Camp, Dresser, and McGee is currently designing a full scale physical-chemical waste treatment facility to serve the industrial concerns in the area. It has also been claimed that activated carbon can be used to remove traces of ethylene bromide from water.[1968] However, activated carbon treatment is of value mainly for the adsorption of organic compounds of relatively high molecular weight and its effectiveness in removing ethylene bromide or methyl chloride from water requires further investigation.

In addition, because of the volatility of methyl bromide and methyl chloride, adequate treatment of waste waters contaminated with small quantities of these compounds could probably be achieved in conventional municipal facilities with aeration.

Disposal/Recovery of Concentrated Wastes

Option No. 1 - Incineration. The complete and controlled high temperature oxidation of halohydrocarbons in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of these compounds with the possibility of recovering the greater part of all of the halogens in some usuable form. In particular, Dow Chemical is currently in the process of designing incinerators to dispose of the concentrated ethylene bromide * and methyl bromide wastes at its Midland Plant.[1970] The off gas from the incinerator will contain both hydrogen bromide and bromine, both of which are harmful pollutants if released to the atmosphere. The hydrogen bromide can be readily removed by scrubbing with caustic soda, but Dow claims to encounter some problems with bromine removal.[1970] However, it is not clear whether Dow has fully investigated the several methods available for the separation of bromine vapors from air: (1) contacting the air-bromine mixture with moist scrap iron leading to the formation of ferrous bromide; (2) absorption in ammonia solution with the formation of ammonium bromide; (3) absorption in ferrous bromide solution with the formation of ferric bromide; (4) alkaline absorption in which bromine reacts with sodium hydroxide or carbonate to form sodium bromate, sodium bromide, and either water or carbon dioxide; (5) lime absorption in which bromine reacts with calcium hydroxide to form calcium bromide and bromate; (6) reduction of bromine by means of sulfur dioxide giving rise to the formation of a spray of fine droplets of hydrobromic and sulfuric acids that could later be trapped by a solution of the same mixed acid circulating in an absorption tower; and (7) absorption with a concentrated solution of sodium bromide

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* Auxiliary fuel will be required in the combustion of ethylene bromide.

cooled below OC in packed towers.[1808] The absorbed bromine that is bound chemically in the form of bromide, bromate or hydrogen bromide can all be recovered by either acidification with sulfuric acid or reoxidizing with chlorine. For small quantities of methyl bromide and ethylene bromide, both compounds could be safely disposed of by dissolution in a flammable solvent and spraying the mixture into the fire box of any incinerator equipped with an afterburner and alkali scrubber. In the case of methyl chloride, combustion units designed for the disposal of chlorinated organic wastes and capable of recovering chlorine in the form of usable hydrogen chloride have been developed, and a 7,000 lb/hr plant is now under construction for E. I. DuPont de Nemours and Company in Victoria, Texas by Union Carbide Corporation.[1743] Properly designed and operated incineration is therefore considered as the best current and near future method for the disposal of concentrated ethylene bromide, methyl bromide, and methyl chloride wastes.

Option No. 2 - Chemical Degradation. The use of chemical reagents to decompose concentrated ethylene bromide, methyl bromide or methyl chloride wastes to less toxic forms has not been specifically reported in the literature. Based on the known reactions of these compounds, however, it appears that: (1) metal alkoxides could be used to react with methyl bromide or methyl chloride leading to the formation of ethers and metallic bromides or chlorides according to the Williamson ether synthesis;[1808] (2) sodium in liquid ammonia could be used to react with methyl bromide or methyl chloride leading to the formation of methane, methylamine, and sodium bromide or chloride; and (3) zinc could be added to ethylene bromide with the formation of ethylene and zinc bromide. Since these methods generally do not lead to the recovery of valuable halogens and little is known of the optimum conditions under which the chemical reagents could be applied, chemical degradation could not be recommended as a technique for the disposal of the halohydrocarbons at the present time.

Option No. 3 - Release to Atmosphere. Methyl bromide is degraded rapidly in the presence of sunlight and air and small amounts of the material could be safely disposed of by slowly releasing the liquified gas to the atmosphere in a well-ventilated outdoor location.[2173]

The disposal of large volumes of ethylene bromide, methyl bromide or methyl chloride wastes in landfill sites, open pits, lagoons and by on-site burning, deep-well disposal, or deep sea burial are not recommended practices because of volatility of these compounds and the obvious contributions to air and water pollution.

To summarize, the only demonstrated method for the removal of the halohydrocarbons from air is refriegerated condensation when these compounds are present in sufficiently high concentrations. The use of MEA, alkaline alkoxide and alcohol scrubbing or activated carbon to remove traces of these halohydrocarbons from air seems feasible, but due to the lack of sufficient supporting data could only be considered as near future waste treatment processes. Adequate methods for the removal of the halohydrocarbons from water include steam stripping, and blowing with air in the case of the more volatile methyl bromide and chloride. Again, activated carbon adsorption to remove traces of these compounds from water could not be considered as a proven method. To dispose of concentrated ethylene bromide, methyl chloride, or large volumes of methyl bromide wastes, the only adequate method is by incineration. Small quantities of concentrated methyl bromide could be safely disposed of by venting to the atmosphere.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Methyl bromide is usually packaged in returnable pressurized cylinders and the empty containers are shipped back to the manufacturers. In addition, residual methyl bromide could be adequately disposed of by careful venting to the atmosphere. Ethylene bromide is mainly used in gasoline formulations, and methyl chloride is generally used as a starting material or as a methylating agent in chemical manufacture. As such, both ethylene bromide and methyl chloride wastes could be adequately handled along with other halohydrocarbon wastes (e.g., chlorinated solvents) from manufacturing plants. The degree of toxicity of all three compounds is moderate when compared with that of the more toxic halohydrocarbons such as carbon tetrachloride. For the above reasons, ethylene bromide, methyl bromide, and methyl chloride are not considered as candidate waste stream constituents for National Dispoal Sites.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ethylene bromide (182)

IUC Name 1,2 -Dibromoethane

Common Names Ethylene dibromide

Structural Formula

$CH_2Br \cdot CH_2Br$

Molecular Wt. 187.88 Melting Pt. 9.3 C (1) Boiling Pt. 131.5 C (1)

Density (Condensed) 2.172 @ 25 C (1) Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

8.5 mm @ 20 C (2) 11 mm @ 25 C (1) 119.9 mm @ 75 C (2)

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 0.43% @ 30 C (1) Hot Water ______ Ethanol Soluble

Others: Completely miscible with carbon tetrachloride, benzene, gasoline, ether, and anhydrous alcohols. (2)

Acid, Base Properties ______

Highly Reactive with aluminum, magnesium, sodium and potassium, strong alkalies, and oxidizing agents. (3)

Compatible with ______

Shipped in glass bottles, 55-gal drums, tank cars (2)

ICC Classification ______ Coast Guard Classification ______

Comments Ethylene bromide is a clear, colorless liquid with a characteristic sweet odor.

References (1) 1618

(2) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Methyl Bromide (267)

IUC Name Bromomethane

Common Names

Structural Formula

CH_3Br

Molecular Wt. 94.95 (1) Melting Pt. -93 C (1) Boiling Pt. 3.6 C(1)

Density (Condensed) 1.732 @ 0 C(1) Density (gas) (Air = 1) 3.27 @ 0 C (1)

Vapor Pressure (recommended 55 C and 20 C)

1250 mm @ 20 C (2) @ @

Flash Point Practically nonflammable (1) Autoignition Temp. 537 C (1)

Flammability Limits in Air (Vol%) Lower 10.0 Upper 15.4 (1)

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water less than 0.1 wt % (1) Hot Water Ethanol Soluble (1)

Others: Soluble in ethyl ether, carbon tetrachloride, chloroform, carbon disulfide, benzene (1)

Acid, Base Properties

Highly Reactive with aluminium, magnesium, and their alloys (1)

Compatible with

Shipped in metal containers or tank cars (rare) (1)

ICC Classification Poisonous Liquid, class B Coast Guard Classification Poisonous liquid, B

Comments Extremely hazardous liquid and vapor under pressure.

References (1) 1810

(2) 1618

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Methyl Chloride (268)

IUC Name Chloromethane

Common Names

Structural Formula

CH_3Cl

Molecular Wt. 50.491 Melting Pt. -97.6 C Boiling Pt. -23.8 C

Density (Condensed) 0.920 @ 20 C Density (gas) (Air = 1) 3.58 @ -15 C

Vapor Pressure (recommended 55 C and 20 C)

101 mm Hg @ -80 F 355.6 mm Hg @ -40 F 1093.6mm Hg @ 5 F

Flash Point Below 0 C Autoignition Temp. 632 C

Flammability Limits in Air (Vol%) Lower 10.7 Upper 17.4

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.46 wt % at 20 C Hot Water 0.26 wt % at 40 C Ethanol soluble

Others: readily soluble in alcohols, chloroform, and mineral oils.

Acid, Base Properties Hydroloyzes in the presence of moisture to hydrochloric acid.

Highly Reactive with aluminum, and to lesser extent with zinc magnesium, the alloys thereof (even when dry), and alkali metals.

Compatible with most other engineering materials.

Shipped in as a liquid under pressure in cylinders and tank cars.

ICC Classification Flammable compressed gas Coast Guard Classification Inflammable gas

Comments Methyl chloride is thermally stable, but also flammable and subject to decomposition upon contact with moisture. **At high temperatures**, it may break down to produce hydrogen chloride and other toxic gases.

References (1) 1811

PROFILE REPORT

Ethylenimine (190)

1. GENERAL

Ethylenimine is a colorless flammable liquid having very high toxicity. It is an extremely reactive compound, the reactivity stemming from the ease with which ring opening occurs due to the strained nature of the three-member ring.[1514]

In June 1963, the Dow Chemical Company announced a new process which used ammonia and ethylene dichloride as raw materials.[1433] With its process, Dow was the first large scale U.S. producer of ethylenimine.[1514] Other commercial facilities for the manufacture of ethylenimine are operated by Borden Inc., Chemirad Corporation, Dow Chemical Company, and Polysciences, Inc.[1670] Physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Ethylenimine is a highly toxic material. It is corrosive to the skin and is readily absorbed in toxic amounts.[1514] It is a skin sensitizer and necrotizing agent.[1492] Liquid ethylenimine is capable of causing a severe burn to the eyes, which may result in partial or total loss of vision. High concentrations of ethylenimine vapor (~100 ppm) may cause eye irritation. This material has a high oral toxicity. Serious illness may result from the ingestion of a relatively small amount.[1514] The inhalation of ethylenimine monomer at a concentration slightly above 25 ppm for 8 hours will kill rats and guinea pigs. In 30 to 60 minutes 250 ppm is dangerous to man.[1492] Available experimental evidence[1514] would indicate that no exposure should exceed 100 ppm regardless of the length of exposure time.

3. OTHER HAZARDS[1514]

Ethylenimine is a highly toxic material and special precautions must be taken when handling or using it. It is extremely flammable in either the liquid or vapor form. Ethylenimine vapors may explode when exposed to electric sparks, static electricity, excess heat, or an open flame.

Undiluted ethylenimine can polymerize violently in the presence of acids or acid-forming materials. Extreme care must therefore be taken to avoid contact with these materials except under controlled conditions such as in the production of polyethylenimine.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Glass, 304 and 316 stainless steels and mild steel are satisfactory materials for handling ethylenimine. Most copper and copper-bearing alloys are not recommended. Silver solder should never be used to fabricate ethylenimine handling equipment, since silver forms an explosive compound with ethylenimine. Almost all rubbers and most plastics are unsatisfactory because of excessive swelling.

Detailed descriptions for ethylenimine handling and transportation are provided by Dow Chemical Company.[1514] It is important that storage tanks be provided with protective and warning devices such as temperature indicators, high-temperature alarms, safety valves, rupture disks and check valves to guard against the dangers of accidentally contaminating the contents of the tank.

Disposal/Reuse

Criteria for disposing of organic ethylenimine waste streams should be in keeping with handling requirements of the highly toxic and flammable material. Incineration of organic waste streams containing ethylenimine should be done under controlled conditions.

The aqueous waste solution should be sent to a holding pond or tank and maintained at or below pH 4 until analysis indicates polymerization is complete.[1514] In this manner the ethylenimine is rendered non-toxic.

Recommended provisional limits for ethylenimine in the environment are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Ethylenimine	0.005 ppm (0.01 mg/M^3)	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Ethylenimine	0.05 ppm (mg/l)	Stokinger & Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Ethylenimine is expected to appear primarily as organic waste streams or as aqueous waste streams in low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs, together with recommendations as to their adequacy.

Concentrated Ethylenimine

It is important that storage tanks be provided with protective warning devices such as temperature indicators, high temperature alarms, safety valves, rupture disks and check valves to guard against the dangers of accidentally contaminating the contents of the tank. Should acidic or reactive contaminants enter the ethylenimine storage tank from a process line or some other source, rapid polymerization or reaction could occur and make it necessary to hurriedly dump the contents of the tank.[1514]

In such a situation, the ethylenimine can be disposed of in two ways. First, it can be mixed with acidic water in an acid scrubber similar to that described by Dow.[1514] The ratio of acidic water to ethylenimine should be about 20:1. The exit scrubber solution should be sent to a covered holding pond or tank. It should be maintained at or below pH 4 until analysis indicates polymerization is complete.

Second, the contents of the ethylenimine storage tank can be pumped directly into a covered pond or holding tank containing an acid solution maintained at pH 4 or less. The polymerization rate can be somewhat increased if mechanical mixing is provided. Regardless of which disposal procedure is utilized the solution should be held in the tank or covered pond until analysis shows polymerization of the ethylenimine to be complete.[1514]

The above procedures are presented as precautionary measures designed to cope with unexpected accidental occurrences. It should be emphasized that if proper protective devices and handling procedures are utilized, emergencies which require rapid disposal of the contents of storage tanks should never occur. Dow has stored and consumed large volumes of ethylenimine for a considerable period of time without experiencing a single emergency incident.[1514]

Dow suggests that the polymer solution can then be pumped directly into the waste stream.[1514] This practice is not recommended because (1) the pH of the solution must first be adjusted to neutral, and (2) it is not certain that the polymer is biodegradable, although other works[0534] describing materials with similar backbones and functional groups support the supposition that it is. It is suggested that further investigation of the biodegradability of the ethylenimine polymer be conducted, and until experimental confirmation is made, this method of disposal should be considered less desirable than incineration discussed below.

Dilute Ethylenimine Waste Streams

Ethylenimine wastes are expected to appear as organic waste streams or as aqueous waste streams. Methods for adequately handling the disposal of dilute ethylenimine waste streams are discussed below.

Dilute Organic Waste Streams. Organic waste streams containing ethylenimine can be adequately disposed of by controlled incineration where oxides of nitrogen are removed from the effluent gas by scrubbers and/or thermal or catalytic devices.[1435]

Dilute Aqueous Waste Stream. Aqueous waste streams containing ethylenimine should be held in a tank or covered pond and maintained at or below pH 4 until analysis indicates polymerization is complete.[1514] The pH is adjusted to 7 and the solution subjected to secondary treatment consisting of aeration and acclimated activated sludge.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Ethylenimine is not considered a candidate waste stream constituent for National Disposal Site treatment. Since this material is so highly reactive a responsive disposal system at the site of occurrence must be available should contaminants enter the concentrated ethylenimine storage tank or tank car and cause rapid polymerization. If the recommended procedure is followed (see the Concentrated Ethylenimine Section), the resulting material may be handled as aqueous waste at the plant site along with any dilute aqueous waste being generated there. Any dilute organic waste streams containing ethylenime should be incinerated at the plant site under controlled conditions discussed in the paragraph or Dilute Organic Waste Streams.

7. REFERENCES

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1570. The Chemical Rubber Company. Handbook of chemistry and physics. 47th ed., Cleveland, 1962. 2,100 p.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ethylenimine (190)

IUC Name

Common Names Azirane(1), Dihydroazirine, Aziridine(2)
Azacyclopropane(2), Dimethylemine(2),
Ethyleneimine(2)

Structural Formula

C_2H_5N

Molecular Wt. 43.07(1)   Melting Pt. -78 C(5)   Boiling Pt. 56 C(1)

Density (Condensed) 0.832 @ 20 C 4 C(1)   Density (gas) 1.48(4) Air=1 @

Vapor Pressure (recommended 55 C and 20 C)

160 mm @ 20 C(4)   756 mm @ 56 C   @

Flash Point 12 F(4)   Autoignition Temp. 612 F(4)

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water Soluble in all proportions(1)   Hot Water   Ethanol Soluble(1)

Others: Soluble in all proportions in most organic solvents(1)

Acid, Base Properties Strongly alkaline(2)

Highly Reactive with Acids, acyl chlorides, amines, ammonia, hydroxy cpds., thiols, hydrogen and many other cpds.(4) Polymerizes easily(2) silver, forms an explosive cpd(4)

Compatible with Glass, Teflon, mild or stainless steel, the following are NOT recommended for use: copper and copper-bearing alloys(4)

Shipped in Glass, mild or stainless steel(4)

ICC Classification III-AGO-WI(4) 4B 240(4)   Coast Guard Classification

Comments Toxicity is very high and handling must be done with great care(4) Mfg.(5) Borden Inc., Chemirad Corp., Dow Chemical Co., and Polysciences Inc.

References (1)	(1570)	(4)	(1514)
(2)	(1492)	(5)	(1670)
(3)	(1571)		

PROFILE REPORT

Glycerol Monolactate Trinitrate (GLTN) (524)

1. GENERAL

GLTN is a powerful, high brisance, liquid explosive with many of the properties of nitroglycerin. The first step in preparation is to esterify glycerol with lactic acid by prolonged heating of a glycerol lactic acid mixture containing 4 percent excess lactic acid. The resulting mixture is then nitrated with a 40:60 mixture of nitric and sulfuric acids maintained at 20 C. Crude GLTN is extracted from this reaction product with ether, neutralized with sodium bicarbonate, washed, and dried with calcium chloride. The product contains about 5 percent nitroglycerin because it is not considered practical to prepare pure GLTN. GLTN is used as a gelatinizer for nitrocellulose.[0474]

The physical/chemical properties for GLTN are summarized in the attached worksheet.

2. TOXICOLOGY

GLTN like nitroglycerin, which is present in GLTN, can cause dilation of blood vessels, headaches, nausea, vomiting, methemoglobinemia, cyanosis, reduced blood pressure, central nervous system depression, coma and respiratory paralysis through inhalation, ingestion or skin absorption. Alcoholic beverages aggravate the health hazard. A Threshold Limit Value (TLV) for GLTN has not been established, but the TLV of 0.2 ppm for nitroglycerin would appear to apply to GLTN.[1142]

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3. OTHER HAZARDS

GLTN is a high explosive that is so sensitive to heat and impact that it undergoes detonation, if confined, when subjected to very mild thermal or mechanical shock by a flame or percussion. It will explode when heated to 223 C.[0474] The material should be handled only by experienced explosive ordnance personnel.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

As in the manufacture of nitroglycerin, wash waters and acid nitrating solutions used in GLTN manufacture must be stored until all GLTN has been decomposed by acid hydrolysis.[0474] Recovery and recycling of the spent acid is possible, after the GLTN has decomposed. Because GLTN is a high explosive it is recommended that no GLTN be released to the environment.

GLTN is stored as a liquid under the DOD regulations for a Class 9 Explosive.[0474] It is not normally shipped as such outside the boundaries of the plant in which it is manufactured. No Department of Transportation (DOT) classification has been assigned to GLTN, and it cannot be shipped via common carrier.

The safe disposal of GLTN is defined in terms of the recommended provisional limits in the atmosphere, and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
GLTN	0.02 mg/M^3*	0.01 TLV*

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
GLTN	0.1* mg/L*	Stokinger and Woodward Method*

---

*Estimated from data for similar compounds

The waste forms containing GLTN are for the most part surplus and obsolete military munitions scheduled for disposal, and manufacturing wastes composed of scrap explosive and explosive-contaminated "inert" materials. (The "inert" materials are almost always combustible wastes--straw, cardboard, paperboard, fiberboard, and the like). The quantities by location of the GLTN, and of the waste forms in which it is contained, are included in the quantities listed under the heading "High Explosives" in the table covering "Explosive Manufacturing Wastes," and under the heading "Propellant, Nitrocellulose Base" in the table for "Obsolete Conventional Munitions" in Volume 14 of this report.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

GLTN which is collected from spills and catch tanks, and that which is considered unsuitable for use (contaminated or unstable to KI test), is currently disposed of by absorption in sawdust, wood pulp or fullers earth, after which it is carefully burned in an open burning area used for explosives disposal. If GLTN is spilled on the ground, the contaminated ground is removed with low-impact tools and burned. Ignition of GLTN is usually accomplished by placing a black powder squib on the surface of the absorbed GLTN. As expected, the products of combustion contain considerable NO_x. This method of disposal is not satisfactory unless, due to the specific character of the waste undergoing treatment, the safety hazards of disposal via the techniques being developed exceed the environmental impact of the NO_x generated by open burning.

Methods currently under investigation for minimum environmental impact, low hazard disposal of nitroglycerin are potentially applicable to the disposal of GLTN. Bacterial degradation and controlled incineration, with afterburners and scrubbing for abatement of NO_x, are two techniques being investigated. Neither of these methods is available for use on GLTN at this time. Additional research is required.

GLTN wastes should be handled only by experienced ordnance disposal personnel with a background in GLTN or nitroglycerin disposal.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

GLTN is not a candidate waste stream constituent for National Disposal Sites, in wastes other than gelatinized nitrocellulose. GLTN, as such, is not normally transported or used outside the complexes where it is manufactured, and facilities for its disposal are available at the sites of manufacture. It is anticipated that GLTN wastes other than gelatinized nitrocellulose will continue to be treated at these facilities. Gelatinized nitrocellulose, as noted in Profile Report (523), is a candidate waste stream constituent for controlled incineration at National Disposal Sites.

7. REFERENCES

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1142. JANAF Hazards Working Group. Chemical rocket propellant hazards. v.2. CPIA Publication No. 194, Silver Springs, Maryland. May 1970.

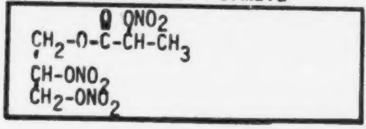
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Glycerol Monolactate Trinitrate (524)

IUC Name

Common Names GLTN

Structural Formula



$$\begin{array}{l} \mathrm{CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{ONO_2}{\overset{|}{C}H}-CH_3} \\ | \\ \mathrm{CH-ONO_2} \\ | \\ \mathrm{CH_2-ONO_2} \end{array}$$

Molecular Wt. 299(1) Melting Pt. Boiling Pt. explodes(1) 223 C

Density (Condensed) 1.47g/cc @ 23 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.01g/100g at 25 C(1) Hot Water <0.015(1) g/100g at 60 C Ethanol

Others: miscible with ether, ether-alcohol, acetone(1)

Acid, Base Properties

Highly Reactive with Hydrolysis takes place in acid solution(1)

Compatible with

Shipped in

ICC Classification not shipped(1) Coast Guard Classification not shipped(1)

Comments

References (1) 0474

PROFILE REPORT

Hydrazine Azide/Hydrazine (527)

1. GENERAL

Hydrazine is widely used as a mono-propellant in rocket engines where the hydrazine is decomposed to expanded volume gaseous products by passage over a catalyst bed. One of the disadvantages of hydrazine as a propellant is that it has a relatively high freezing point (1.5 C). Blends of hydrazine azide and hydrazine have lower freezing points than hydrazine and these blends improve rocket performance (Specific Impulse) which has led to much experimental activity with these blends. The lowest freezing point (-17.5 C) is obtained for the blend containing 77 percent hydrazine by weight.[2338] It is this blend that will be discussed in this Profile Report.

Hydrazine azide/hydrazine blends have been prepared by at least three methods. The first method involves the reaction of sulfuric acid with sodium azide to form hydrazoic acid which is discharged into hydrazine to form hydrazine azide. The second method involves the metathesis of sodium azide and hydrazine sulfate to form hydrazine azide and sodium sulfate. The third method involves the reaction of butyl alcohol and sodium azide to give hydrazine azide and C_4H_5OHNa.[2169,2238] The first method is preferred, since the hydrazine azide is prepared in an excess of hydrazine which makes the process very simple and eliminates waste streams.[2338] The third method was abandoned because of low yields and the second method gave a product contaminated with sodium sulfate that reduced the activity of decomposition catalyst beds.

Though small quantities of hydrazine azide/hydrazine blends have been prepared and shipped, it is doubtful that these blends will become an item of commerce because these blends have been found to be very corrosive to stainless steel.

The physical/chemical properties for a hydrazine azide/hydrazine blend containing 77 percent hydrazine are summarized on the attached worksheet.

2. TOXICOLOGY

The toxicology of hydrazine azide/hydrazine blends has not been evaluated. Since hydrazine is the major component of the blends, it can be assumed that the toxicity will be at least equal to that for hydrazine (see Profile Report on Hydrazine [212]). A worker at TRW Systems who inhaled the vapors from a 1-gram sample of a blend for a few minutes in the laboratory reported a detached feeling that left in about two hours. It is therefore recommended that exposure to inhalation and skin contact with vapors of the blends be avoided until the toxicity is defined.

3. OTHER HAZARDS

Hydrazine azide/hydrazine blends will present the same fire hazards as hydrazine. These are discussed in the hydrazine Profile Report (212). Impact tests indicate the binary system hydrazine azide/hydrazine is not sensitive to 120Kg-cm of shock with one exception. A detonation did occur on the second bounce when testing one sample saturated with hydrazine azide. Also, no detonation propagation could be demonstrated for the blends.[2338]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Adequate procedures for the safe handling, transportation and storage of the blends have not been defined because the blends are regarded as an experimental material. On one occasion 10-lb quantities in a polyethylene container packed in a wooden box were shipped as a Corrosive Liquid under a white label. Because hydrazine azide/hydrazine blends attack stainless steel, it is doubtful that additional quantities will be shipped for evaluation as a monopropellant.

Personnel who are required to handle wastes containing or contaminated with hydrazoic acid/hydrazine blends should wear rubber protective clothing, and use forced air supply respiratory equipment. Hydrazine azide/hydrazine blends will probably be encountered only as excess or contaminated material.

The safe disposal of hydrazine azide/hydrazine is defined in terms of the recommended provisional limits in the atmosphere, in potable water, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Hydrazine	0.013 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrazine	0.065 mg/l	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Because blends of hydrazine azide/hydrazine are an experimental material, disposal processes have not been established. It is recommended that material be disposed of by incineration. The blends should be diluted with water and sprayed into an incinerator with a scrubber similar to that used for hydrazine (see Profile Report on Hydrazine [212]).

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because only experimental quantities of hydrazine azide/hydrazine blends have been prepared, it is not likely that any of the blends will be sent to National Disposal Sites for disposal. If at some future date the blends are manufactured, then wastes containing the blends will be candidates for National Disposal Sites. The techniques for disposal, as discussed in Section 5, will be similar to those used for disposal of hydrazine wastes.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrazine Azide/Hydrazine (527)

IUC Name Hydrazinium Azide/Hydrazine

Structural Formula

N_5H_5-N_2H_4

Common Names

Weight ratio: 77 parts N_2H_4, 23 parts N_5H_5

Molecular Wt. a blend not a compound(1) Melting Pt. -17.5C(1) Boiling Pt.

Density (Condensed) 1.083 g/cc @ 25 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

7.7 torr @ 20 C(1) 23.5 torr @ 40 C(1) 520 torr @ 55 C(1)

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water soluble(1) Hot Water soluble(1) Ethanol slightly soluble(1)

Others:

Acid, Base Properties

Highly Reactive with oxidizing agents(1)

Compatible with glass, polyethylene(1)

Shipped in polyethylene enclosed in a wood box(1)

ICC Classification corrosive liquid(1) Coast Guard Classification -

Comments Experimental monopropellant, not produced commercially

References (1) 2338

PROFILE REPORT

Hydroquinone (220)

Hydroquinone is a white crystalline solid of moderate to high toxicity. It is widely distributed in nature as a component of the glucoside arbutin, found in the leaves of many plants.[1433] Its performance as a reducing agent provides the basis for its widespread use as a photographic developer and antioxidant.

There are a number of patented processes for the manufacture of hydroquinone but the method employed by the Eastman Chemical Products Division of Eastman Kodak, in Kingsport, Tennessee, is believed to be representative of those which are of commercial importance.[1679] The process used at Kingsport is essentially a three-step operation.[1679] In the first step aniline is oxidized to quinone in the presence of an excess of manganese dioxide and sulfuric acid. In the second step, quinone is steam distilled from the reaction liquor and immediately brought into contact with a water suspension of iron dust that reduces the quinone to hydroquinone. The third step is the purification of hydroquinone to the quality desired.

Hydroquinone is available in technical and photographic (higher purity) grades and is shipped in 100- and 325-lb (net) fiber drums.[1433] In addition to Eastman, the other domestic producers of technical grade hydroquinone are Carus Chemical Company, Diamond Shamrock Corporation, and the DuPont Company.[1718] Their combined production during 1970 was approximately 13.6 million lb.

The principal large-scale use of hydroquinone is as a reducing agent in photographic developers.[1433] For this application it is used in dilute aqueous solution; a common concentration is 10 g in a liter of developer.[1686] It is also employed as an antioxidant in a variety of products including

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rubber and edible fats and oils.[1433] The antioxidant activity of hydroquinone is also the basis for its use as a polymerization inhibitor (stabilizer) for reactive vinyl monomers.[1433] When used as an antioxidant-stabilizer hydroquinone or its derivatives generally comprise less than 2 percent of the materials involved.[1433]

The physical/chemical properties of hydroquinone are summarized in the attached worksheet.

2. TOXICOLOGY[0766, 1492]

Under normal conditions of use, (low concentrations, moderate temperatures, closed systems, etc.) hydroquinone does not present a serious hazard. However, ingestion of relatively large quantities of material is potentially dangerous. For example, the ingestion of 1 g by an adult has been reported to cause nausea, vomiting, a feeling of suffocation, shortness of breath, cyanosis, convulsions, delirium and collapse. Death has followed the ingestion of 5 g of the material. Many of these symptoms may be attributable to the strong excitation effect of hydroquinone on the central nervous system.[1433]

Skin contact may result in dermatitis, although the actual causitive agent may be quinone, formed by the oxidation of hydroquinone in the presence of moisture.[1679] Quinone may also be responsible for the corneal staining and opacification which has occurred in workers exposed for prolonged periods to concentrations of vapor not high enough for the production of systemic effects.

A Threshold Limit Value (TLV) of 2 mg/M^3 of air has been recommended for this material.

3. OTHER HAZARDS

Hydroquinone is considered to be only a slight fire and explosion hazard when exposed to fire or heat.[0766] However, such exposure may release toxic fumes.

Caution should be exercised when contacting hydroquinone with strong oxidizing agents, since it is a potent reducing agent. A highly exothermic reaction with sodium hydroxide has also been reported.[1569]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The safe handling and use of hydroquinone requires that care be taken to avoid prolonged exposure to its dust and vapor through use of dust masks and gloves. Careful design of equipment to prevent leaks during manufacture and use, and adequate ventilation are very important.[1569] To further minimize exposure during the manufacturing process, Eastman[1569] requires that employees be rotated through various operations in the department and that uniforms be changed and showers taken at the end of each workday.

Hydroquinone is shipped in 100-and 325-lb fiber drums which do not require special hazardous material labels.[0766]

In general, the precautions necessary to prevent the contamination of hydroquinone and thus guard its economic value are adequate to assure its safe handling.

Disposal/Reuse

Purification of hydroquinone by recrystallization is a normal phase of the manufacturing process[1679] and hydroquinone users with the required equipment may employ this technique to recover slightly contaminated material.

An adequate process for the disposal of hydroquinone must include provisions for limiting the evolution of dust and vapors and the opportunity for oxidation to the more volatile and toxic quinone. The problem of dust and vapor is probably not a serious one, since almost all hydroquinone waste is in the form of dilute aqueous solutions of hydroquinone or, in the case of spent photographic developer, hydroquinone monosulfinate.[1686] Oxidation to quinone is not rapid in acidic or neutral solutions and can be prevented in the presence of another reducing agent such as sodium sulfite which is present in photographic developers.[1686]

Aqueous waste solutions are amenable to common municipal secondary waste treatment processes.[1686] The hydroquinone molecule, containing only carbon, hydrogen and oxygen atoms, can also be burned in a properly designed and operated incinerator.

Recommended provisional limits for hydroquinone in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Hydroquinone in air	0.02 mg/M^3	0.01 TLV
Hydroquinone in water and soil	0.10 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The preferred processing options for the disposal of hydroquinone wastes are briefly described in the following paragraphs together with judgments as to their adequacy.

Option No. 1 - Waste Water Treatment

The major portion of hydroquinone wastes are expected to be in the form of dilute aqueous solutions. Hydroquinone can be effectively removed from such waste streams by conventional secondary sewage treatment (biochemical oxidation) methods. Of those processes, activated sludge is the most efficient, with aerated lagoons or trickling filters equally effective if sufficient residence time for complete decomposition is available.[1686]

Anaerobic processes (faculative ponds) are not recommended for hydroquinone waste streams which contain components incorporating sulfur atoms (e.g., photographic process effluents) because of the danger of H_2S production.

Concentrated hydroquinone wastes may also be treated by common municipal secondary waste water treatment methods after adequate dilution. The required dilution will depend upon the capacity of the treatment plant in question; hydroquinone exerts a BOD of 1.12 lb/lb of waste.[1686]

The direct introduction of untreated hydroquinone wastes into surface or underground waters is not recommended because of the known high toxicity of the material to fish and other fauna.

Option No. 2 - Incineration

Incineration of hydroquinone in a well designed and operated incinerator is an acceptable waste disposal method. Hydroquinone should be combusted at a minimum temperature of 1,800 F for a minimum of 2.0 seconds. Care must be taken to avoid leakage of unburned hydroquinone vapors, and to remove harmful combustion products (e.g., SO_2, NO_x) produced by other components in the waste mixture.

The incineration option is most applicable to concentrated hydroquinone wastes and in areas removed from ready access to appropriate municipal or private secondary treatment facilities.

Option No. 3 - Land Burial

Landfill or deep well disposal of hydroquinone waste streams is not generally recommended because of the danger of release of this water-soluble, toxic substance to the environment. In addition to possible leaching of hydroquinone by rain or subterranean water, its possible oxidation to the more toxic, volatile, and less biodegradable quinone must be considered as contraindicative for burial disposal methods. However, a landfill meeting California Class I requirements is adequate. (See Volume 3, Landfill Disposal Process Description.)

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Hydroquinone is not a candidate waste stream constituent for disposal at National Disposal Sites. Waste streams containing this material can be effectively and safely disposed of, at or near the sites of waste generation, by conventional waste water treatment of controlled incineration.

7. REFERENCES

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1686. Personal communication. L. E. West, Eastman Kodak Company, to H. E. Green, TRW Systems, May 9, 1972.

1718. United States Tariff Commission. Synthetic organic chemicals, United States production and sales, 1970. TC publication 479. Washington, U.S. Government Printing Office, 1972. 262 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydroquinone (220)

IUC Name 1,4-dihydroxybenzene

Common Names (1) 1,4-benzenediol, quinol, hydroquinol

Structural Formula

HOC_6H_4OH

Molecular Wt. 110.1 Melting Pt.(1) 170.5 C Boiling Pt.(1) 286.2 C

Density (Condensed) (1) 1.358 @ 20/4 C Density (gas) (2) 3.81 @ Air = 1

Vapor Pressure (1) (recommended 55 C and 20 C)

1 mm @ 132.4 C ____ @ ____ ____ @ ____

Flash Point (1) 329 F (cc) Autoignition Temp. (1) 960 F

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility (2)

Cold Water 5.8g/100g solution @ 15 C 9.4g/100g solution @ 28.5 C Ethanol Very soluble

Others: Ether

Acid, Base Properties Neutral

Highly Reactive with Oxidizing agents (2), sodium hydroxide (3)

Compatible with ____

Shipped in Fiber drums (4)

ICC Classification ____ Coast Guard Classification ____

Comments Source (5): Allied Chem., Diamond Shamrock, Eastman Chemical Products, Mallinckrodt Chemical Works, J. T. Baker Chemical Co., Carus Chemical Co.

References (1) 0766 (4) 1679

(2) 1433 (5) 1571

(3) 1569

PROFILE REPORT

Maleic Anhydride (249)

1. GENERAL

Maleic anhydride is a toxic solid at room temperature, appearing as white rombic needles in the crystalline form. The products of commerce are shipped as flakes, briquettes and as a liquid at temperatures between 55 and 60 C.[1497] Most of the maleic anhydride produced commercially is made by the catalytic oxidation of benzene in the vapor phase.[1433] It is primarily used in polyester resins, lesser quantities being used to make fumaric acid, agricultural chemicals, alkyd surface coatings, lubricants, copolymers, and plasticizers.[1316]

As of 1970, large scale commercial facilities for the manufacture of maleic anhydride (production greater than 20 million lb annually) were operated by six companies, Monsanto producing 75 million lb of the 237 million lb produced annually.[1506] Physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Maleic anhydride is a strong irritant to the skin, eyes and the mucous membrane. It is very irritating to the eyes and can cause painful conjunctivitis and possible corneal dullness. If it is left in contact with the skin, painful irritation can result, particularly if the skin is moist.[1433] Oral ingestion may cause death or permanent injury after very short exposure to small quantities.[0766] A detailed description of personnel protective equipment is provided by the Manufacturing Chemists Association Inc.[1497] for handling both the solid and molten material. Toxicological effects in man are characterized by a Threshold Limit Value (TLV) of 0.25 ppm (1 mg/M^3).

3. OTHER HAZARDS

Maleic anhydride is an irritant to the skin and mucous membrane especially in the presence of moisture.[1497] It is also a moderate fire hazard when exposed to heat or flame.

This material emits toxic fumes when heated and can react on contact with oxidizing materials[0766] such as the alkali metals or amines at temperatures above 150 C. The flammable limits (by volume) are 1.4 percent to 7.1 percent.[1497] It is recommended that the material not be heated above 70 C[1570] since the closed cup flash point is 102 C.[1497]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Precautions must be taken to guard against health and fire hazards whenever maleic anhydride is handled. Although maleic anhydride does not present a severe fire hazard,[1433] it is recommended that spark-resistant tools be used in handling the material and explosion venting be provided in general construction of equipment and buildings in which flammable vapors or dusts are liable to concentrate.[1497]

Maleic anhydride is shipped as flakes, briquettes and in the molten form. Briquettes and flaked maleic anhydride are packaged and shipped in multiwall paper bags, fibre drums and metal drums. Molten maleic anhydride is shipped in tank cars and tank trucks constructed of mild or stainless steels.[1497]

A description of personnel protective equipment to be used when handling maleic anhydride is available from the Manufacturing Chemists Association, Inc.[1497] This includes a discussion of eye, respiratory, head and body protection.

Disposal/Reuse

Most of the maleic anhydride produced commercially is made by the catalytic oxidation of benzene in the vapor phase.[1433] It is also obtained as a byproduct in the oxidation of naphthalene and from butylenes by catalytic vapor-phase oxidation similar to the benzene process.[1501] The catalytic vapor-phase oxidation is a continuous process having no contact with water[1499] since water is not used or generated in the process. Hence, any contamination of water would probably stem from the washdown of equipment, such as storage tanks or tank cars, and clean up of spills. This in itself does not present a major problem since maleic anhydride is easily hydrolized by water to maleic acid which is readily soluble in water and may be easily neutralized with sodium hydroxide. The resultant dilute aqueous solution will generally exhibit no evidence of toxicity, taste or odor problems in the context of disposal to municipal or industrial treatment plants. This neutralized solution is readily oxidized biologically.[1497]

Maleic anhydride and maleic acid are found as dilute wastes in the tars which appear as bottoms products from the vacuum columns in the manufacturing processes. One manufacturer[1502] currently disposes of this waste in a privately owned sanitary landfill. Test wells surround the landfill to check migration of any material. The tars are also used as boiler feed in some plants[1499] thus disposing of the material by incineration.

Any method of maleic anhydride disposal must be evaluated with respect to its environmental impact. Recommended provisional limits of maleic anhydride in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Maleic Anhydride in Air	0.0025 ppm (0.01 mg/M^3)	0.01 TLV
Maleic Anhydride in Water and Soil	0.05 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Maleic anhydride is expected to appear in low concentrations in tars produced during manufacture. It is anticipated that it will also be present as maleic acid in water used to clean up spills or equipment. Concentrated maleic anhydride waste will appear as contaminated or off grade product. Generally, the contamination will be caused by hydrolysis[1499] or the material will be discolored making it unfit for use in some manufacturing processes. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Maleic Anhydride

Essentially, four options are available for the disposal of concentrated maleic anhydride wastes. These are recycle, incineration, landfill and deep sea burial.

By far, the most appropriate method of disposal of concentrated maleic anhydride wastes is to recycle the material. This is accomplished either by locating a consumer willing to use low grade material or by reprocessing the material at the plant for captive use.[1499] If recycling is impossible, controlled incineration is the disposal method of choice. Incineration must be controlled to ensure that the waste maleic anhydride, as well as any other material in the waste stream, is completely oxidized to nontoxic combustion products.

The use of landfills for the disposal of concentrated maleic anhydride wastes should be considered only when the options of recycle and incineration are impractical and the landfill is of the California Class I type. The use of deep sea burial is not recommended since injury to aquatic life is possible and once dumped, control of the material is lost.

Dilute Waste Streams

The following sections will discuss the methods used to dispose of waste streams containing maleic anhydride in dilute form.

Option No. 1 - Secondary Treatment. Waste water containing maleic acid from maleic anhydride equipment wash downs can be adequately handled in municipal sewers after neutralization of the dilute solution. Once neutralized by NaOH addition and in dilute aqueous solution there is no evidence of toxicity, taste or odor problems in the context of disposal to municipal or industrial treatment plants since the sodium maleate (in dilute form) is readily oxidized biologically.[1497]

Option No. 2 - Incineration. Incineration of the tar byproducts containing maleic anhydride is an adequate means of disposing of this material particularly since the tars can be used as fuel in boilers.[1944] Care must be taken to ensure that complete oxidation of the maleic anhydride, as well as any other materials in the waste stream, is attained.

Option No. 3 - Sanitary Landfill. Sanitary landfills are currently used to dispose of tars containing maleic anhydride and maleic acid.[1502] This method is recommended only when the landfill utilized meets California Class I landfill standards since this will minimize the possibility of water contamination.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Maleic anhydride is not judged to be a candidate waste stream constituent requiring National Disposal Site treatment since the various waste forms containing this material can be treated at the site of generation with common industrial and municipal techniques. Also, some concentrated maleic anhydride wastes, depending on other waste stream constituents, are particularly well suited for recycling and this is currently being done.[1499]

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Maleic Anhydride (249)

IUC Name

Common Names Toxilic Anhydride(3), cis-butenedioic Anhydride3

Structural Formula

$C_4 H_2 O_3$

Molecular Wt. 98.06 Melting Pt. 56 C Boiling Pt. 197-9 C(1)

Density (Condensed) 1.314 @ 60 C Density (gas) 3.4(3) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm Hg @ 44 C @ @

Flash Point 218 F (c/c)(3) Autoignition Temp. 890 F(3)

Flammability Limits in Air (Vol. %) Lower 1.4 Upper 7.1

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Soluble Hot Water Decomposes to the acid Ethanol

Others: Soluble in Ether, Acetone, Chloroform

Acid, Base Properties

Highly Reactive with Alkali Metals, amines, any oxidizing agent

Compatible with Mild Steel, Stainless Steel, Aluminum

Shipped in Drums and tank cars when liquid; paperbags, drums when solid

ICC Classification 20, 28 Coast Guard Classification

Comments Mfg.: Allied Chem. Corp.; Ciba Products Co.; Eastern Color. & Chem. Co.; Monsanto Co.; Tar Residuals Inc.; USS Chemicals;(2)

References (1) 1570
(2) 1571
(3) 0766

PROFILE REPORT

Manganese Methylcyclopentadienyltricarbonyl (502)

1. GENERAL

Production

There is one producer of manganese methylcyclopentadienyltricarbonyl ($CH_3C_5H_4Mn(CO)_3$) in the United States, the Ethyl Corporation, which produces an undisclosed amount at its Orangeburg, South Carolina plant.(2128,2177) Ethyl owns at least six patented processes for the production of $CH_3C_5H_4Mn(CO)_3$[1433] of which only one is currently in use.[2177] Methylcyclopentadiene is reacted with metallic sodium to form methylcyclopentadienylsodium. This in turn is reacted with manganese chloride to yield biscyclopentadienylmanganese plus sodium chloride. The mixture is scrubbed with oil and water and the resultant pure biscyclopentadienylmanganese is reacted with carbon monoxide to yield the manganese methylcyclopentadienyltricarbonyl. The final product contains traces of manganese cyclopentadienyltricarbonyl, which are considered acceptable.[2174]

Use

At present, $CH_3C_5H_4Mn(CO)_3$ is used as an additive to distillate type fuel oils to improve combustion under the trade name CI-2. The utilities industries have found it particularly useful for reducing the opacity of their stack gases.[2176] As a fuel component it is combusted completely to the manganese oxides.

The Ethyl Corporation hopes to expand its use considerably as an anti-knock additive to gasoline (trade name AK-33X) to replace lead tetraethyl.[2128] It is anticipated that, beginning with the 1975 model year, cars will have to be equipped with catalytic afterburners to satisfy the projected pollution requirements. At present, all proposed catalysts are poisoned by lead, but not by manganese; hence the interest in $CH_3C_5H_4Mn(CO)_3$. Projected additions range from 0.025 to 0.05 g Mn/gal. gasoline as Mn metal, compared to the present addition of 2.3 to 2.4 g Pb/gal. gasoline as Pb metal. At

$2.10/lb in tank car quantities, however, it is not economically competitive with lead tetraethyl at present.[2175]

It has been experimentally determined[2176] that all Mn that would be emitted from automobile exhausts would be in the form of the oxides. The $CH_3C_5H_4Mn(CO)_3$ is unstable with respect to sunlight, and decomposes slowly to a brown flocculent material. No chemical analysis has ever been performed on these decomposition products.[2176,2177]

2. TOXICOLOGY

Health and Safety Standards

The HEW 1971 Annual List of Toxic Substances[1312] reports that 0.12 mg/m^3 of manganese cyclopentadienyltricarbonyl produced symptoms of pulmonary disorder and disorders of the central nervous system in man. The mode of entry was by inhalation. Since the methylcyclopentadienyltricarbonyl is chemically similar to the cyclopentadienyltricarbonyl, it is reasonable to assume that manganese methylcyclopentadienyltricarbonyl would produce the same effects.

Epidemiology

Since the reported symptoms of manganese cyclopentadienyltricarbonyl poisoning are the same as those reported for manganese metal poisoning, i.e., pulmonary disorders and impairment of the central nervous system, it is reasonable to assume that the mechanisms are similar. It is generally believed that manganism is caused by enzyme inhibition in the central nervous system. $CaNa_2$ EDTA administered intravenously provides relief in the early stages of disease; prolonged chronic illness is essentially incurable. The epidemiology of manganese poisoning is discussed more fully in the Profile Report on Manganese (499).

On the basis of experimental evidence,[2197,2198] Russian workers suggest an LD50 of 150 mg/kg for white mice and an LD50 of 80 mg/kg for white rats for manganese cyclopentadienyltricarbonyl. Administration was by direct insertion into the gastrointestinal tract. In addition to the symptoms of manganism, extensive hemolysis was found in the subject animals. It is postulated that this was due to cyclopentadiene which split off the original molecule.

3. OTHER HAZARDS

Manganese methyclopentadienyltricarbonyl is flammable with a flash point in excess of 200 F.[2176] It decomposes slowly in sunlight to unidentified products whose potential hazards cannot be evaluated until such time as they are characterized.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Manganese methylcyclopentadienyltricarbonyl is a flammable liquid of relatively low vapor pressure (0.08 torr at 20 C) and high flash point (greater than 200 F).[2176] As a component of gasoline, the maximum anticipated concentration is 0.20 g/gal. or 0.05 g Mn/gal gasoline as Mn metal.[2128] $CH_3C_5H_4Mn(CO)_3$ must be stored in opaque containers, for it is decomposed by sunlight to a brown flocculent material of unknown composition.[2174,2177] Otherwise, it remains quite stable below its flash point, which is in excess of 200 F. It should be shipped in steel drums or tank cars,[2175] suitably labeled as a Class B poison, flammable liquid.

Disposal/Reuse

When distillate fuels or gasoline containing $CH_3C_5H_4Mn(CO)_3$ are combusted, the only manganese compounds released are mixtures of the oxides.[2128] Field studies of stack emissions from stationary sources indicated concentrations of 0.1 to 0.2 $\mu g/m^3$ 1,000 ft downwind (compared to 0.01 to 0.2 $\mu g/m^3$ background) and 0.03 to 0.05 $\mu g/m^3$ 1,500 ft downwind (compared to 0.02 $\mu g/m^3$ background). On-site soil samples contained 12 to 109 ppm Mn, while off-site soil samples contained 28 to 61 ppm Mn. The samples may have been contaminated with indigenous coal dust which runs 1,000 ppm Mn.[2194]

Since the toxic effects of manganese methylcyclopentadienyltricarbonyl are believed to be due to its manganese component, the acceptable criteria for its release to the environment are defined in terms of the following provisional limits.

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Manganese Methylcyclopentadienyltricarbonyl in Air	0.05 mg/M^3 as Mn	0.01 TLV for Mn
Manganese Methylcyclopentadienyltricarbonyl in Water and Soil	0.05 ppm as Mn	Drinking Water Standard for Mn

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

As an additive to gasoline or other fuels, $CH_3C_5H_4Mn(CO)_3$ compares very favorably to lead tetraethyl. It has a lower vapor pressure (0.08 torr vs. 0.47 torr at 20 C), a lower anticipated concentration in gasoline (0.20 g/gal. vs. 3.75 g/gal. for $Pb(C_2H_5)_4$), and is probably somewhat less toxic (symptoms induced in man at 0.12 mg/M^3 vs. a Threshold Limit Value (TLV) for $Pb(C_2H_5)_4$ of 0.075 mg/M^3). Its handling, storage, and transportation under its classification as a Class B poison, flammable liquid, are adequate at present and for the foreseeable future.

Its susceptibility to decomposition under the action of sunlight is widely known, and the producer and users exercise care that it not be exposed. The decomposition products have not been characterized, however, so any possible hazards associated with decomposition cannot be evaluated at this time.[2193,2195,2174,2176,2177]

Currently, the addition of 2.3 to 2.4 g Pb/gal gasoline as $Pb(C_2H_5)_4$ provides a maximum urban air concentration of 2.3 μg/m^3,[2106] or 1/100 of the TLV for Pb.[0766] If it is assumed that lead tetraethyl is replaced completely by manganese methylcyclopentadienyltricarbonyl in the concentration of 0.025 to 0.05 g Mn/gal. gasoline,[2128] then the Mn air level from automobile exhausts will be approximately fifty times less than the present Pb level, or 1/1250 of the TLV for Mn. It is unlikely that this would present a health hazard, notwithstanding the apparent lack of safety margin in the present TLV of 5 mg/m^3 for Mn.

The Chemistry and Physics Branch of the U.S. Environmental Protection Agency[2195] is sponsoring an experimental study of $CH_3C_5H_4Mn(CO)_3$ additions to gasoline, which will be conducted by the Dow Chemical Company. Initial results are expected in November 1972. Similarly the Chemistry and Physics Branch will soon begin a joint study with the U.S. Navy on the consequences of $CH_3C_5H_4Mn(CO)_3$ additions to jet fuel used in engine overhauling and testing.

Production of Manganese Methylcyclopentadienyltricarbonyl

There are two waste streams associated with the production of manganese methylcyclopentadienytricarbonyl by the Ethyl Corporation in its Orangeburg, South Carolina facility: an oil soluble stream, and a water soluble stream.[2177] These streams are treated individually and there are several options available for each one.

Oil Soluble Stream

Option No. 1 - Incineration of the Oil Stream and Venting to the Atmosphere. This is the present procedure. Any organic manganese compounds present are converted to the oxides. There is no monitoring of manganese emissions, although state requirements with regard to opacity, SO_2, and oxides of nitrogen are being met consistently. It is necessary to determine the emission level of manganese before an evaluation can be made with regard to the adequacy of this option.

Option No. 2 - Incineration of the Oil Stream and Wet Scrubbing of the Exhaust Gases. If it is determined that manganese emissions from the incinerator cause the Threshold Limit Value of 5 mg/M^3 to be exceeded within the plant or the provisional limit of 0.05 mg/M^3 to be exceeded outside of the plant, a wet scrubber could be installed to bring the air emissions to an acceptable level. The effluent from the scrubber could be combined with the water soluble waste stream.

Water Soluble Stream

Option No. 1 - Discharging the Water Stream Into the Local River. This is the present procedure. It is probably unsatisfactory since the effluent runs 4.2 mg Mn/l and the U. S. Public Health Service recommends a maximum Mn concentration of 0.05 ppm in drinking water. However, the plant influent which is derived from ground water, runs 2.6 mg/l. If the river water contains significant manganese (close to the limit) this technique is not adequate.

Option No. 2 - Precipitating the Manganese in a Settling Pond Prior to Discharging into the Local River. If the manganese contained in the effluent is indeed objectionable, it can be precipitated quite easily by temporary storage of the effluent in a settling pond in which the pH is adjusted within the range 8.5 to 9 by the addition of lime. Water of this pH would meet USPHS specifications with regard to pH and would be essentially manganese-free.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

At present, manganese methylcyclopentadienyltricarbonyl does not constitute a hazard or threat to the general public. The manganese oxides resulting from its combustion as a gasoline additive would not constitute an air pollution problem, and would represent a considerable improvement over the combustion products of the lead tetraethyl currently in use.

The handling, storage, and transportation of $CH_3C_5H_4Mn(CO)_3$ are adequate at present and for the foreseeable future, providing the manufacturer's admonitions to avoid exposure to sunlight are obeyed. The photochemical decomposition of $CH_3C_5H_4Mn(CO)_3$ has been observed, but not characterized. There is a small, but finite chance that poisonous manganese carbonyls are evolved.[2181,2195] It is recommended that the decomposition products be characterized in a laboratory setting.

It is recommended that a determination be made of manganese air emissions resulting from the incineration of the oil soluble waste stream at the Ethyl Corporation's production facility at Orangeburg, South Carolina. If it is found that the emissions exceed recommended levels, a wet scrubbing unit should be installed to remove them. The effluent from the scrubbing unit could then be mixed with the water soluble waste stream.

The plant influent at 2.6 mg Mn/l is already considerably higher than the U. S. Public Health Service recommended Drinking Water Standard of 0.05 mg/l. It is raised to 4.2 mg/l within the plant. These values have been reported to the U. S. Army Corps of Engineers and the Environmental Protection Agency.[2177] If it is desired to reduce the Mn content, the addition of lime in a settling pond would prove a simple expedient. The precipitation of the manganese would not involve the creation of any volatiles.

Manganese methylcyclopentadienyltricarbonyl can be handled quite adequately at the industrial level and is therefore not a candidate waste stream constituent for national disposal.

7. REFERENCES

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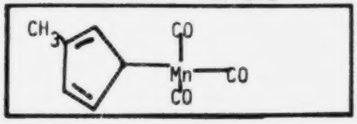
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Manganese methylcyclopentadienyltricarbonyl (502)

Common Names CI-2, AK-33X

Structural Formula



Molecular Wt. 218 (1) Melting Pt. 1.5 C (2) Boiling Pt. 228.6 C

Density (Condensed) 1.3884 g/ml @ 20 C Density (gas) @ (extrapolated)

Vapor Pressure (recommended 55 C and 20 C)

0.08 mm Hg @ 20 C 9.3 mm Hg @ 100 C @

Flash Point > 200F Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water insoluble Ethanol soluble

Others: most organic solvents

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in steel drums (1 gal, 5 gal, 55 gal) tank cars (4000, 6000, 8000 gal)

ICC Classification Class B poison, flam. liquid **Coast Guard Classification**

Comments decomposes in sunlight to unidentified products

References (1) 2176
(2) 2176

PROFILE REPORT

Nitroaniline (300)

1. GENERAL

The nitroanilines are yellowish crystaline substances described as being highly toxic.[0766] They comprise three possible position isomers; 2-(mp:71 C), 3-(mp:112 C), and 4-nitroaniline (mp:146 C).[1492] All three isomers have been used as dyestuff intermediates, although pigments using 4-nitroaniline have now been virtually supplanted by inorganic pigments and other more lightfast materials.

2-Nitroaniline is prepared by ammonalysis of ortho-nitrochlorobenzene or by nitration and desulfonation of sulfanilic acid. It is used to prepare a few azo and anthraquinone dyes.[1433] 3-Nitroaniline is prepared by partial reduction of 1,3-dinitrobenzene. It is used in organic synthesis and as a dye intermediate.[1433] 4-Nitroaniline is prepared by ammonolysis of 4-nitrochlorobenzene or by nitration of acetanilide followed by hydrolysis.[1433] Its principal uses and their approximate share of production are: rubber antioxidant, 40 percent; gasoline additives, 20 percent; dyes and pigments, 20 percent; pharmaceuticals and veterinary, 7 percent; agricultural chemicals, three percent; miscellaneous, 10 percent.[1506]

Commercial facilities for the manufacture of 4-nitroaniline are operated by American Aniline (2 X 10^6 lb/yr), Monsanto (10^7 lb/yr), and Universal Oil (3 X 10^6 lb/yr). Southern Dyestuff Company makes limited quantities for captive use.[1506] Sources for the 2- and 3-isomers may be found in OPD Chemical Buyers Guide.[1571]

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2. TOXICOLOGY [1498]

Nitroaniline is a hazardous material because of its ability to produce cyanosis upon absorption into the body. Significant adsorption may occur either by inhalation of the dust or from contact with the skin. While skin exposure may be hazardous, the rate of absorption through the intact skin is relatively low. Nitroaniline is mildly irritating to the eyes and may cause some cornea damage. A value of 1 ppm by volume or 6 mg/M^3 in air has been suggested as the maximum allowable concentration considered safe for an 8-hr exposure.

3. OTHER HAZARDS

Nitroaniline is a moderate fire hazard when exposed to heat or flame or when chemically reacted with oxidizers.[0766] Contact with the skin and eyes, as well as the inhalation of vapors and dust should be avoided.[1498]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Nitroaniline is not a serious industrial hazard if workers are adequately instructed and supervised in proper methods of handling the chemical. Whenever possible, nitroaniline should be handled within a wholly closed system. Equipment should be designed to avoid spills and to prevent dust from escaping into the air.[1498]

A description of personnel protective equipment and instructions on its use are recommended by the Manufacturing Chemists Assn.[1498] The Department of Transportation (DOT) regulations are very detailed and specific concerning packages which may be used to transport nitroaniline (see Section 73.365 and 73.373 of the DOT regulations). Under the DOT regulations, nitroaniline is classified as a Class B poison.

Disposal/Reuse

Disposal or reuse of waste nitroaniline streams must take into account the toxic nature of these materials. It is assumed that dilute aqueous waste streams containing nitroaniline are treated in the same manner as dinitrophenol waste streams, i.e., secondary treatment using acclimated activated sludges and aeration (see Profile Report on Dinitrophenol [164]).

Recommended provisional limits for nitroaniline in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis of Recommendation
Nitroaniline in air	0.01 ppm (0.06 mg/M^3)	0.01 TLV
Nitroaniline in water and soil	0.30 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Nitroanilines are expected to appear primarily as aqueous waste streams in low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Nitroanilines

In the event it becomes necessary to dispose of a significant quantity of concentrated nitroaniline, and purification/recycling is impractical, then incineration of nitroaniline is the recommended method of disposal. Qualified personnel familiar with handling toxic materials must be available. The material must be incinerated under controlled conditions where oxides of nitrogen are removed from the effluent gas by scrubbers and/or thermal or catalytic devices.[1435] Combustion should be carried out at a minimum temperature of 1,800 F for at least 2.0 seconds.

Dilute Aqueous Waste Streams

Nitroanilines appear as aqueous waste in the manufacturing process. It is assumed that methods used to dispose of aqueous nitroaniline waste are similar to methods used for dinitrophenol, i.e., secondary treatment utilizing activated sludges. The adequacy of this practice is in doubt due to the apparent difficulty of microorganisms to degrade aromatic nitro compounds.[1044] Until data are available to show that nitroanilines can be degraded satisfactorily in secondary treatment facilities, it is recommended that aqueous waste streams be concentrated and treated as discussed in the section on concentrated nitroanilines.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The nitroanilines do not appear to be candidate waste stream constituents for National Disposal Sites. It is anticipated that the great majority of the aqueous nitroaniline waste generated in the chemical industries will continue to be treated at the source of the waste generation, but it is recommended that emphasis should be changed from biological treatment processes to concentration and subsequent controlled incineration until the adequacy of the biological processes is proven. In the event concentrated material becomes contaminated, it can be incinerated as discussed in the section on concentrated nitroanilines.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroaniline (O) (300)

IUC Name 2-nitroaniline

Common Names ortho-nitroaniline

Structural Formula

$C_6H_6N_2O_2$

Molecular Wt. 138.13(1) Melting Pt. 71.5 C(1) Boiling Pt. 284 C(1)

Density (Condensed) 1.442(1) @ 15 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1mm(2) @ 142.4 C 28mm(1) @ 165 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility(1)

Cold Water very slight Hot Water slight Ethanol slight, very (hot)

Others: very, benzene, $CHCl_3$ acetone

Acid, Base Properties basic, forms water sol. salts with acids(2)

Highly Reactive with acids

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments dye-stuff intermed(2)

References (1) 1570

(2) 1492

(3) 1571

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroaniline (n)

IUC Name 3-nitroaniline

Common Names meta-nitroaniline

Structural Formula

$C_2H_2N_2O_2$

Molecular Wt. 138.13(1) Melting Pt. 114 C(1) Boiling Pt. 305-7 C(1) (decomp)

Density (Condensed) 1.430 @ 4 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.16 mm(1) @ 100C @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1g/800 ml(2) Hot Water Ethanol 1g/20 ml(2)

Others: 1g/11.5 ml (MeOH)(2) $CHCl_3$(1)

Acid, Base Properties Forms water soluble salts with mineral acids,(2) very slightly basic(4)

Highly Reactive with acids

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Toxic-absorbed through skin,(2) dye intermediate,(2)

Suppliers: American Cyanamid, Conray Products, Aceto Chemical Co.

References (1) 1570

(2) 1492

(3) 1571

(4) 1655

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroaniline (p)

IUC Name 4-nitroaniline

Common Names para-nitroaniline

Structural Formula

$C_6H_6N_2O_2$

Molecular Wt. 138.13(1) Melting Pt. 148.5-9.5 C(1) Boiling Pt. 331.7 C(1)

Density (Condensed) 1.424 @ 20 C Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

0.03 mm @ 106 C ____ @ ____ ____ @ ____

Flash Point 390 Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water 1g/1250 ml Hot Water 1g/45 ml Ethanol 1g/25 ml

Others: Ether (1g/30 ml)

Acid, Base Properties Basic - forms water sol. salts mineral acids(3)

Highly Reactive with ____

Compatible with ____

Shipped in ____

ICC Classification Poison B Coast Guard Classification Poison B

Comments Very toxic.(3) dyestaff intermediate.(3) suppliers:(4) Sherwin Williams Chemical, Fallek Chemical, American Hoechst Corp. (organic inter)

References (1) 1570
(2) 0766
(3) 1492
(4) 1571

PROFILE REPORT

Nitrobenzene (301)

1. GENERAL

Nitrobenzene is a pale yellow liquid with a distinct almond-like odor. It is highly toxic when ingested, inhaled, or absorbed through the skin. The most important application of nitrobenzene is in the manufacture of aniline for the synthesis of dyestuffs. At least 85 percent of the nitrobenzene manufactured in the United States is used by the dye industry. Other uses of nitrobenzene are for the manufacture of rubber chemicals, photographic chemicals and drugs.[1433,1316]

The present industrial use of nitrobenzene as a starting material for dyestuffs and other organic intermediates stems largely from the impetus provided by its ease of manufacture. The current method for the commercial manufacture of nitrobenzene is the direct nitration of benzene using mixed sulfuric and nitric acids.[1433]

Large scale commercial facilities for the manufacture of nitrobenzene are operated by Allied, Cyanamid, First Chemical, Mobay, Monsanto, and Rubicon.[1506] Physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Nitrobenzene exhibits the high toxicity typical of nitroaromatic compounds. It is readily absorbed by contact with the skin, inhalation of the vapor, or by ingestion.[1433] The maximum allowable concentration in air is 1 ppm (5 mg/M^3).[0766] The ready absorption of nitrobenzene through the skin is the major potential hazard in handling this material. Significant absorption continues as long as the oily liquid remains on the skin surface or as long as contaminated articles of clothing are worn.[1494] The Hygienic Guide Series states that nitrobenzene may be almost immediately fatal if large areas of the body are in contact with the liquid or if massive concentrations are inhaled.

The odor of nitrobenzene can usually be detected without difficulty in concentrations of 0.05 ppm in the atmosphere.[1513] Nitrobenzene, soluble in water to the extent of 0.19 parts nitrobenzene in 100 parts water at 20 C,[1513] is odorous in water at low concentrations; 0.03 mg/l has been reported as the the Threshold Limit Value.[1494] Acute aquatic toxicity occurs at about 30 mg/l.[1494] The lethal dose orally in rabbits is 700 mg/kg.[1492]

3. OTHER HAZARDS

Nitrobenzene is a hazard to health due to its high toxicity and is considered to be a moderate fire and explosion hazard when exposed to heat or flame.[1433] This material is classified by the Department of Transportation (DOT) as a "Poisonous Liquid" Class B and each shipping container must bear the DOT poison label. The handling of nitrobenzene should be carefully controlled with precaution and procedures such as the use of protective clothing, face protection and adequate ventilation. The lower explosive limit in air is 1.8 percent by volume at 200 F, the upper limit has not been reported.[1494]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Nitrobenzene is highly toxic when absorbed through the skin, inhaled as vapor, or swallowed. Although the vapor given off at elevated temperatures is flammable, nitrobenzene can be handled with little danger of fire since the flash point of the liquid (88 C) is much higher than the temperatures at which it is normally handled.[1494] Containers specified for nitrobenzene are listed in the Code of Federal Regulations, Title 49, paragraphs 173.345 and 173.346. Usual containers are as follows:

Spec. 5, 5A, 5B, or 5C metal barrels or drums,

Spec. 17C or 17E single-trip metal drum containers,

Spec. 15A, 15B, 15C, 16A or 19A - wooden boxes with glass or earthenware inside containers,

Spec. 103, 103W, 103A or 103A-W - tank cars,

Spec. MC300, MC301, MC302, MC303 or MC305 - tank motor vehicles.

Detailed handling instructions for small containers, drums, tank trucks and tank cars are supplied by the Manufacturing Chemists Assn.,[1494] along with personnel protective equipment.

Disposal/Reuse

Nitrobenzene is prepared by the direct nitration of benzene, using a nitric acid-sulfuric acid mixture.[1501] The batch process utilizes reaction vessels specially built of cast iron or steel and fitted with agitators. Newer plants use a continuous process, as typified by the Biazzi process, for the production of nitrobenzene. The sequence of operations is essentially the same as in the batch process, the main differences being the use of smaller reaction vessels, lower nitric acid concentrations, and higher reaction rates.[1433]

The reduction of nitrobenzene to aniline outranks all other uses of nitrobenzene as an industrial chemical, only 15 percent of the nitrobenzene produced is for other uses.[1501] Both Mobay[1521] and Rubicon[1519] utilize all their nitrobenzene production at the manufacturing site. Waste streams associated with the manufacturing process are aqueous in nature and are given primary and secondary treatment consisting of treatment with lime and digestion with activated sludge before being discharged into waterways. Treatment facilities are in operation for handling aqueous nitrobenzene waste streams that reduce the BOD loading 90 percent to 95 percent.[1520]

Recommended provisional limits for nitrobenzene in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Nitrobenzene in air	0.01 ppm (0.05 mg/M^3)	0.01 TLV
Nitrobenzene in water and soil	0.25 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Nitrobenzene is expected to appear primarily as aqueous waste streams in low concentrations and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Nitrobenzene

In the event it becomes necessary to dispose of significant quantities (55 gal. drum or 10,000-gal. tank car) of concentrated nitrobenzene, two disposal options are available. The first option is to contact the manufacturer and determine if it is possible to return the material. E. I. duPont de Nemours[1432] has indicated a willingness to accept concentrated nitrobenzene for reprocessing provided the contaminant or contaminants in the nitrobenzene are compatible with their reprocessing system and the economic aspects of the situation are favorable. The second option is incineration since nitrobenzene is flammable and amenable to the treatment. Combustion should be carried out at a minimum temperature of 1,800 F for at least 2.0 seconds.

Small amounts of nitrobenzene can be adequately disposed of by dilution provided proper secondary treatment facilities have organisms acclimated to this material (see section on Dilute Aqueous Waste).

The open burning of nitrobenzene is not an adequate means of disposing of this material since oxides of nitrogen as well as incomplete combustion products may be generated during its combustion. Controlled combustion processes where the oxides of nitrogen are scrubbed from the effluent gas or where a thermal or catalytic device[1435] is used to reduce the oxides of nitrogen to their elemental form is acceptable.

Although landfill techniques are used extensively throughout the chemical industry, it is recommended that this practice be continued only when landfills meet California Class I requirements.

Dilute Aqueous Waste

Nitrobenzene appears as waste in water at concentrations in the order of parts per million.[1501,1521] Waste treatment facilities are in operation that handle nitrobenzene aqueous waste[1521] and some waste water treatment facilities combine both plant aqueous wastes and domestic sewage.[1520] In the latter case, effluent from the plant is given primary treatment, followed by treatment with lime to adjust the pH from 2.5 to 7. The effluent is mixed with municipal sewage and allowed to equilibrate one day after which it is lagooned for 20 hours with mechanical aeration. BOD reduction runs from 90 percent to 95 percent. Secondary treatment utilizing acclimated[0534] activated sludge systems for nitrobenzene aqueous waste should be adequate.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that systems to handle the great majority of the aqueous nitrobenzene waste generated in the chemical process industries will continue to be located at the source of the waste generation. For concentrated nitrobenzene waste, it will not be necessary to have a specific facility at a National Disposal Site provided: (1) it can be recycled, or (2) incinerated in a safe manner (see section on Concentrated Nitrobenzene) at the manufacturers' site.*

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*However, incinerators designed for handling other organic wastes (at National Disposal Site) will be capable of handling Nitrobenzene.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitrobenzene (301)

IUC Name Nitrobenzene

Common Names Nitrobenzene, Nitrobenzol, Oil of Myrbane

Structural Formula

$C_6H_5NO_2$

Molecular Wt. 123.11 Melting Pt. 5.7 C(1) Boiling Pt. 210.9 C

Density (Condensed) 1.19867 @ 25/4 C(1) Density (gas) 4.75(1) @

Air = 1.0

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 44.4 C(4) 22 mm @ 100 C(4) 50 mm @ 120 C(4)

Flash Point 87.8 C (C.C.)(4) Autoignition Temp. (900 F(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 1.8% at 200 F(1) Upper

Solubility

Cold Water Slightly(2) 0.19/100 parts water(4) Hot Water 1.0/100 parts water at 200 C(4) Ethanol Very soluble

Others: ether, benzene (very)

Acid, Base Properties

Highly Reactive with Highly flammable

Compatible with any metal container is usually satisfactory, paraffin or plastic drum liners should not be used.(5)

Shipped in tank cars, tank truck, steel drums.(4)

ICC Classification Coast Guard Classification DOT Reg. 73.346(5)

Comments Sources:(3) A.I.D. Chemical Co., Inc; Allied Chemical Corp; American Cyanamid Co; E. I. duPont de Nemours & Co., Inc; First Chemical Corp; McKesson Chemical Co; Metchler Chemical Co. Inc.

References (1) 0766 (4) 1513
(2) 1570 (5) 1572
(3) 1571

PROFILE REPORT

meta- and para-Nitrochlorobenzene (302)

1. GENERAL

Nitrochlorobenzene (meta and para) are yellow crystals having melting points of 46 C and 82 C, respectively.[1492] Both materials are highly toxic and have similar effects on the body. Their effects are analogous to those of nitrobenzene.[0766]

Mononitrochlorobenzenes can be obtained from benzene by a combination of nitration and halogenation. The order of the operations determines the positional isomer content of the product. meta-Nitrochlorobenzene is obtained by nitration of benzene followed by chlorination. By reversing the order, a mixture results containing about two parts of the para isomer to one of the ortho. On a technical scale, fairly sharp separation of the isomers resulting from nitration is made by freezing out the bulk of the higher-melting para compound, fractionating the liquid portion, and further freezing.[1655]

Domestic production of p-nitrochlorobenzene was reported as over 88.9 million lb for the year of 1970.[1718] Production figures are not available for the meta compound. Manufacturers of the meta compound are E. I. du Pont de Nemours and Company Incorporated[1718] and Universal Oil Products.[1718] The para compound is manufactured by American Aniline Products,[1718] E. I. du Pont de Nemours Company Incorporated,[1718] Monsanto Company,[1718] and Universal Oil Products.[1718]

2. TOXICOLOGY[0766]

Intoxication from these materials can be serious. When absorbed, they form methenoglobin and give rise to cyanosis and blood changes. Their effects are analogous to those of nitrobenzene (See Profile Report on nitrobenzene [301]). They can cause poisoning by the pulmonary route and their effects are cumulative. The toxic hazard rating for ingestion and inhalation is high for both materials.

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3. OTHER HAZARDS

In industry it is the dust of these materials that is most often the source of intoxication.[0766] Protective goggles, gloves and breathing masks capable of removing airborne dust should be worn when working with these materials in the open. There is only a moderate fire hazard associated with the nitrochlorobenzenes.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Gloves and chemical goggles should be worn to protect the hands and eyes when handling nitrochlorobenzene flakes or crystals. A breathing mask capable of eliminating nitrochlorobenzene dust is recommended when handling these materials in other than fume hoods or closed systems.

The nitrochlorobenzenes (meta and para) are shipped as crystals and flakes according to Department of Transportation (DOT) regulations.[0278] They are classed as "Poison B" and require a poison label on all packages.

These materials should be stored in tightly closed containers away from heat or flame. When heated to decomposition, they emit highly toxic fumes of oxides of nitrogen and phosgene.[0766] They can also react with oxidizing materials.

Disposal/Reuse

A definition of acceptable criteria for the disposal of meta and para-nitrochlorobenzenes must also take into account acceptable criteria for the release of hydrogen chloride, hydrochloric acid, and nitrogen oxides to the environment, since current practice in nitrochlorobenzene disposal involves some processes that reduce nitrochlorobenzene to these materials.[1432]

Current disposal techniques utilize incineration and land burial. These methods are acceptable provided the recommended provisional limits in nitrochlorobenzene, hydrogen chloride, hydrochloric acid and nitrogen oxides in the environment are not exceeded. The recommended provisional limits are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
_p_-Nitrochlorobenzene in air	0.01 mg/M^3	0.01 TLV
_m_-Nitrochlorobenzene in air	0.01 mg/M^3	Based on p-Nitrochlorobenzene
Hydrogen chloride in air	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Hydrochloric acid in air	0.05 ppm (0.07 mg/M^3)	0.01 TLV
Nitrogen oxides in air	0.05 ppm (0.07 mg/M^3)	0.01 TLV
_p_-Nitrochlorobenzene in water and soil	0.05 ppm (mg/l)	Stokinger and Woodward method
_m_-Nitrochlorobenzene in water and soil	0.05 ppm (mg/l)	Based on p-Nitrochlorobenzene

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The nitrochlorobenzenes are expected to appear primarily as dilute organic waste streams and to a much lesser degree as dilute aqueous waste and concentrated waste. The processing options are briefly described in the following paragraph together with recommendations as to their adequacy.

In the event it becomes necessary to dispose of a significant quantity of concentrated nitrochlorobenzene, two adequate disposal options are available. The first option is to incinerate the material. It is expected that either a rotary kiln or liquid combustor, depending upon the form of the waste, followed by secondary combustion and aqueous or caustic scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second.

The chloride abatement problem may be simplified by insuring against elemental chlorine formation through injection of steam or methane into the combustion process. The nitric oxides may be abated through the use of thermal or catalytic devices. The second option is to bury the material in a California Class I type landfill. It is recommended that dilute organic waste be disposed of by incineration. Concentration followed by incineration is the recommended method of disposing of dilute aqueous waste.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The nitrochlorobenzenes are expected to appear primarily as dilute organic waste and to a much lesser degree as dilute aqueous waste and concentrated waste. Processes for handling the disposal of these wastes will be located at manufacturing sites and/or industrial disposal facilities and represent common industrial technology. Therefore, these compounds are not judged to be candidate waste stream constituents for National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name m-nitrochlorobenzene (302)

IUC Name 1-chloro-3-nitrobenzene(1)

Common Names m-chloronitrobenzene (1)

Structural Formula

$C_6H_4ClNO_2$

Molecular Wt.(1) 157.56 Melting Pt.(1) 44 C Boiling Pt. 235-6 C(1)

Density (Condensed) 1.534 @ 20/4 C(2) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble(1) Hot Water Ethanol Slightly soluble(1)

Others:(1) Soluble in ether benzene CS_2 chloroform acetic acid

Acid, Base Properties

Highly Reactive with Can react with oxidizing materials(2)

Compatible with Glass, metals, earthenware(3)

Shipped in

ICC Classification Poison B(3) Coast Guard Classification

Comments Mfg. by:(4) E. I. du Pont de Nemours and Company Incorporated; Universal Oil Products

References (1) 1570 (4) 1718
(2) 0766
(3) 0278

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name p-nitrochlorobenzene (302)

IUC Name 1-chloro-4-nitrobenzene(1)

Common Names p-chloronitrobenzene(2)

Structural Formula

$C_6H_4ClNO_2$

Molecular Wt.(1) 157.56 Melting Pt.(1) 83 C Boiling Pt.(1) 242 C

Density (Condensed) 1.520 Density (gas)

Vapor Pressure (recommended 55 C and 20 C)

Flash Point 127 C(2) Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble(1) Hot Water Ethanol Slightly soluble(1)

Others:(1) Soluble in ether , CS_2

Acid, Base Properties

Highly Reactive with

Compatible with Glass, metals, earthenware(3)

Shipped in

ICC Classification Poison B(3) Coast Guard Classification

Comments Mfg. by:(4) American Aniline Products Incorporated; Monsanto Company.

References (1) 1570 (4) 1718

(2) 0766

(3) 0278

PROFILE REPORT
ON NITROPARAFFINS

Nitroethane (303), Nitromethane (308), 1-Nitropropane (311)

1. GENERAL

Introduction

The nitroparaffins treated in this report have all been selected as probable candidate waste stream constituents for industrial disposal. These materials are similar in that they are commodity chemicals made by the same process with relatively low toxicity, well-defined and safe methods of industrial handling and common methods of disposal. The nitroparaffins are, therefore, discussed as a class in this report.

Manufacture and Use[1433,1501]

The major method of manufacture of nitroparaffins is by the reaction of propane with nitric acid in the molar ratio of 1 to 5 at 390 to 400 C and 100 to 125 psi. All four lower nitroparaffins are produced by varying the conditions and the relative amounts can be adjusted somewhat to meet market demands.

$$C_3H_8 + HNO_3 \longrightarrow CH_3NO_2(10\text{-}30\%) + C_2H_5NO_2(20\text{-}25\%)$$

$$+ [CH_3\text{-}CH(NO_2)\text{-}CH_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2]\ (55\text{-}65\%)$$

The nitroparaffins are used as intermediates in the production of nitro alcohols, alkanolamines, polynitro compounds, and hydroxylamine and its salts. Other major uses are as cosolvents for polymers, extraction or partition solvents, reaction media, recrystallization solvents and other minor solvent uses. Smaller amounts of nitroparaffins are used in high explosives, as special purpose additives in gasoline and diesel fuels, and as a stabilizer for halogenated alkanes.

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Physical and Chemical Properties

The physical and chemical properties discussed in this report are included in the attached worksheets.

2. TOXICOLOGY[0766,1433]

The nitroparaffins are classified by most toxicologists as slightly toxic in marked contrast to the aromatic nitrocompounds. The chief industrial hazard is by inhalation. High concentrations of nitroparaffin vapors produce a mild irritation of the respiratory tract and early symptoms of intoxication such as headache or nausea, which disappear promptly when exposure is reduced. Large doses may cause methemoglobinemia, cyanosis and injury to the liver and kidneys. Repeated skin contact does not cause allergies or other adverse physiological effects.

The Threshold Limit Values (TLV) and Maximum Allowable Concentrations are listed below. The values for the nitropropanes are thought to be very conservative.[1433]

Nitroparaffins	TVL ppm	 mg/M^3	MAC ppm
Nitromethane	100	250	100
Nitroethane	100	310	100
1-Nitropropane	25	90	-
2-Nitropropane	25	90	-

3. OTHER HAZARDS[0766,1433,1569]

The mononitroparaffins are relatively stable, but impact under confined conditions can cause explosion of nitromethane. A combination of high temperature and pressure can cause nitromethane to act as a monopropellant. Alkaline solutions of the nitroparaffins should not be reduced to dryness since the metal salts are explosive.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation

The nitroparaffins are toxic to a certain extent by inhalation and, for this reason, should be handled in a well-ventilated area. Respirators are recomended when necessary. Although accidental contact is not dangerous to the skin, good technique requires that it be kept to a minimum.[0766,1433]

Commercial-grade nitroparaffins are shipped and stored in ordinary carbon steel. However, wet nitroparaffins containing more than 0.1 to 0.2 percent water may become discolored when stored in steel for long periods, even though corrosion of the steel is not excessive. Aluminum and stainless steel are completely resistant to corrosion by wet nitroparaffins.

Storage of nitroparaffins in contact with lead or copper or alloys containing these metals should be avoided. Polymeric materials for gaskets, hoses, etc., should be tested for their suitability before exposure to nitroparaffins.

The commercial nitroparaffins have flash points greater than 100 F and hence do not require a U.S. Department of Transportation (DOT) red label. The ignition temperatures of the lower homologs are relatively high for organic solvents. When ignited, nitromethane burns with a lazy flame, which often dies out spontaneously, and in any case is readily extinguished with water which floats on the heavier nitromethane. The nitropropanes burn more vigorously, but less so than gasoline.

Since nitromethane can explode under conditions of heat, shock and pressure, it preferably should be stored in the 55-gal. drums in which it is shipped. These containers are of lightweight construction so that there is little possibility that they might develop sufficiently high internal pressure either to ignite the nitromethane or to allow it to burn as a monopropellant. Bulk-storage tanks should be isolated, buried, or barricaded to protect them from projectile impacts should an explosion occur in nearby equipment or facilities. With the exception of nitomethane, there are no restrictions on shipment or storage of the lower mononitroparaffins. Nitroethane or the nitropropanes in unconfined quantities have not been exploded by heat and/or shock applied under extreme test conditions.

Disposal/Reuse

Commercial manufacturers who use nitroparaffins as chemical intermediates, generally reuse all unreacted materials. Manufacturers who use nitroparaffins in various solvents recycle them indefinitely. When used in explosives or as a fuel, they are completely combusted.

Recommended provisional limits for the nitroparaffins discussed in this report are listed below.

Contaminant in Air	Provisional Limit ppm	Provisional Limit mg/M^3	Basis for Recommendation
Nitromethane	1.0	2.5	0.01 TLV
Nitroethane	1.0	3.1	0.01 TLV
1-Nitropropane	0.25	0.90	0.01 TLV
2-Nitropropane	0.25	0.90	0.01 TLV

Contaminant in Water and Soil	Provisional Limit ppm or mg/l	Basis for Recommendation
Nitromethane	12.5	Stokinger and Woodward Method
Nitroethane	15.5	Stokinger and Woodward Method
1-Nitropropane	4.5	Stokinger and Woodward Method
2-Nitropropane	4.5	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Recycling

Presently, manufacturers who use nitroparaffins as solvents or chemical intermediates recycle all possible material. This is the method of choice.

Option No. 2 - Incineration

Unusable nitroparaffins that are unfit for recyling can be incinerated. The incineration of large quantities of material may require NO_x removal by catalytic or scrubbing processes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The wastes generated by the industries that use nitroparaffins can be handled on site by recyling and common incineration methods. They should not be considered as candidate waste constituents requiring National Disposal Site treatment.

7. REFERENCES

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1569. Manual of hazardous chemical reactions. Boston National Fire Protection Association, 1971. 308 p.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroethane (303)

IUC Name nitroethane

Common Names

Structural Formula

$CH_3-CH_2-NO_2$

Molecular Wt. 75.07

Freezing Pt. -90 C(1)

Boiling Pt. 114.0 C(1)

Density (Condensed) 1.052 @ 20/20 C(1) Density (gas) 2.58(1) @

Vapor Pressure (recommended 55 C and 20 C)

15.6 mm @ 20 C(1) @ @

Flash Point 82 F(1)
106 F(2)

Autoignition Temp. 778 F(1)

Flammability Limits in Air (wt %) Lower 4.0%(2) Upper

Explosive Limits in Air (wt. %) Lower 3.4%(1) Upper

Solubility

Cold Water 4.5 g/ml(200)(2) Hot Water Ethanol miscible(2)

Others: miscible, methanol, ether;(2) soluble, chloroform, alkaline aq. solution.(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766
(2) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroparaffins (309)

IUC Name

Common Names class of compounds including C_1-C_3 compounds.

Structural Formula

See 309a, 309b, 303, 311.

Molecular Wt.   Melting Pt.   Boiling Pt.

Density (Condensed) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point 103-120 F(1)   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water   Hot Water   Ethanol

Others:

Acid, Base Properties slightly acidic; salts of inorganic bases may be explosive.(1)

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments the nitroparaffins are dangerous when heated in confined containers.

References (1) 0766

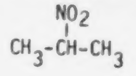
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroparaffins (309)

IUC Name 2-nitropropane

Common Names

Structural Formula



$$CH_3\text{-}\overset{NO_2}{CH}\text{-}CH_3$$

Molecular Wt. 89.09 Freezing Pt. -93 C(1) Boiling Pt. 120 C(1)

Density (Condensed) 0.992 @ 20/20 C(1) Density (gas) 3.06 @

Vapor Pressure (recommended 55 C and 20 C)

10 mm @ 15.8 C(1) @ @

Flash Point 103 F(1) Autoignition Temp. 802 F(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 2.6% Upper

Solubility

Cold Water 1.7 Ml/100 ml(2) Hot Water Ethanol miscible(3)

Others: miscible with many organic solvents.(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766

(2) 1492

(3) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nitroparaffins (309)

IUC Name nitromethane

Common Names nitrocarbol

Structural Formula

CH_3-NO_2

Molecular Wt. 61.04 Freezing Pt. -29 C(1) Boiling Pt. 101 C(1)

Density (Condensed) 1.130 @ 20/4 C(1) Density (gas) 2.11 @

Vapor Pressure (recommended 55 C and 20 C)

27.8 mm @ 20 C(1) @ @

Flash Point 95 F(1) Autoignition Temp. 785 F(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 7.3% Upper

Solubility

Cold Water 9.10%(2) Hot Water Ethanol soluble(2)

Others: soluble - ether, dimethylformamaide.(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Forms an explosive sodium salt which bursts into flame on contact with water.

References (1) 0766

(2) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 1-Nitropropane (311)

IUC Name 1-nitropropane

Common Names

Structural Formula

CH_3-CH_2-CH_2-NO_2

Molecular Wt. 89.09 Freezing Pt. -108 C(1) Boiling Pt. 132 C(1)

Density (Condensed) 1.003 @ 20/20 C(1) Density (gas) 3.06 @

Vapor Pressure (recommended 55°C and 20°C)

7.5 mm @ 20 C(1) @ @

Flash Point 120 F(1) Autoignition Temp. 789 F(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 2.6% Upper

Solubility

Cold Water 1.4 ml/100 ml(2) Hot Water Ethanol miscible(3)

Others: miscible with many organic solvents(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766
(2) 1492
(3) 1570

PROFILE REPORT

AROMATIC NITRO COMPOUNDS
4-Nitrophenol (310), 4-Nitrotoluene (312)

1. GENERAL

Introduction

The aromatic nitro compounds treated in this report have been selected as probable candidate waste stream constituents for industrial disposal. The materials are similar in that they are commodity chemicals with similar toxicity, well-defined methods of industrial handling and common methods of disposal. These compounds are, therefore, discussed as a class in this report.

Manufacture and Use[1433]

The aromatic nitrophenols can be made by both direct and indirect routes. However, phenol because of its hydroxyl group is both readily nitrated and oxidized making a nitration by the conventional nitric acid route uneconomical. Consequently, commercial routes utilize indirect two-step procedures. The preferred technique is the hydrolysis of the corresponding nitrochlorobenzene with 15 percent sodium hydroxide at 160 C.

The nitrophenols are used as intermediates in the preparation of dyestuffs, plant sprays (parathion), aminophenols and photochemicals.

The nitrotoluenes are manufactured by the direct nitration of toluene in either batch (liquid phase) or continuous (gas phase) processes. Care must be used to prevent an accumulation of excess nitric acid as this will oxidize toluene reducing the yield and at the same time producing explosive tetranitromethane. A typical product mixture contains 62 to 63 percent

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o-nitrotoluene, 3 to 4 percent m-nitrotoluene and 33 to 34 percent p-nitrotoluene. The reaction product is washed free of acid and distilled into ortho-, meta-, and para-rich fractions.

The nitrotoluenes are used principally in the synthesis of dyes such as new magenta and turquois blue.

Physical and Chemical Properties

The physical and chemical properties of the compounds discussed in this report are included in the attached worksheets.

2. TOXICOLOGY[0766,1433,1492]

As a class, the nitrophenols are very toxic compounds not only when ingested but also when inhaled or absorbed through the skin. The characteristic effects of poisoning are an enhancement of metabolism with a rise in body temperature, headache, heavy sweating, thirst, fatigue and just before death a sudden rise in body temperature. Chronic exposure is often characterized by hyperthermia, methemoglobinemia, depression, liver and kidney damage, cataracts, eczema, inflammation of the lymphatic glands and degeneration of the nails. The para-isomer is the most toxic of the three mononitrophenols.

The toxic properties of the nitrotoluene are similar to those of nitrobenzene but less pronounced. Poisoning can occur by ingestion, inhalation and skin absorption and is characterized by headaches, drowsiness, nausea, vomiting and in severe repeated cases, methemoglobinemia with cyanosis, liver injury and jaundice.

The Threshold Limit Value (TLV) and Maximum Allowable Concentration that have been established are:

Substance	TLV		MAC
	ppm	mg/M^3	mg/M^3
p-nitrophenol	--	--	4
p-nitrotoluene	5	30	--

3. OTHER HAZARDS

No special hazards other than those mentioned elsewhere in this report are connected with the manufacture and use of these compounds.[0766,1433,1492,1569]

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation[0766,1433]

The nitroaromatic hydrocarbons treated in this report are all very toxic by inhalation, ingestion or skin contact. These materials should only be handled in well-ventilated areas and protective clothing and respirators are recommended where necessary. The toxic nature of these compounds is such that all unnecessary contact with these compounds should be avoided. In case of accidental contact, all contaminated clothing should be removed instantly and the skin washed thoroughly with soap and water. Bicarbonate solutions will help in the removal of the nitrophenols. A change of clothing may be necessary after handling large amounts of these compounds.[0766,1433]

Storage should be in a cool, dry, well-ventilated area, away from acute fire hazards.

These materials are shipped under a variety of U. S. Department of Transportation (DOT), U. S. Coast Guard and International Air Transport Association (IATA) regulations. Since all the compounds treated in this report have flash points above 100 C (212 F), none require DOT warning labels for hazardous chemicals. The primary danger in shipping is due to toxicity and information on safe handling and use of these compounds can be found in the Chemical Data Sheets published by the Manufacturing Chemists Association, standard reference sources, or manufacturers Technical Data Sheets.

Disposal/Reuse

Recommended provisional limits for the nitro compounds discussed in this report are listed below.

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Nitrophenol in air	0.002 mg/M^3	Based on similar compounds
Nitrotoluene in air	0.05 ppm (0.30 mg/M^3)	0.01 TLV
Nitrophenol in water and soil	0.010 ppm (mg/l)	Based on similar compounds
Nitrotoluene in water and soil	1.50 ppm (mg/l)	Stokinger and Woodward Method

The manufacture of nitrophenols and nitrotoluenes produces a dilute stream of waste water from a washing or precipitation step. The streams can be either acid or alkaline. A small amount of distillation bottoms is also produced.

The Manufacturing Chemists Association Chemical Data Sheet SD-21 for a nitrobenzene[2479] suggests that small quantities can be disposed of by open burning or as slurry by flushing down the sewer. Disposal of larger quantities by landfill in areas reserved for toxic wastes is suggested.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Treatment of Waste Water to Reduce Biological and Chemical Oxygen Demand

The nitrophenols and nitrotoluenes are biodegradable to acclimated activated sludges. In addition, microorganisms are very sensitive to shock by these compounds and release of abnormal amounts can cause failure of an activated sludge treatment plant.[1543,2479] For these reasons, it is recommended that waste streams be treated on site. Discharge of partially treated waste water should be done only with approval of the local municipal treatment plant and in a continuous, low level manner.

Option No. 2 - Incineration

Contaminated material that cannot be reclaimed is best disposed of by controlled incineration. The toxic nature of these compounds requires extreme care to maintain complete combustion at all times. Incineration of large quantities may require the use of scrubbers and/or thermal or catalytic devices[1435] to control the level of effluent oxides of nitrogen.

Option No. 3 - Flushing Small Quantities Down the Sewer as a Slurry

This alternative is suggested by the Manufacturing Chemists Association for nitrobenzene and would presumably also be applicable to the nitrotoluenes.[2479] It should not be considered as a valid method of disposal since accumulation of nitrotoluene or nitrotoluene vapors in drains and/or sewers could pose a serious hazard to unsuspecting personnel. In addition, insufficient dilution could cause damage to activated sludge sewage treatment plants.

Option No. 4 - Landfill of Large Quantities of Nitrotoluene at Special Toxic Wastes Landfill Sites

This method is suggested by the Manufacturing Chemists Association for nitrobenzene and should also be applicable to the nitrotoluenes.[2479] This method of disposal is not considered adequate unless the landfills are of the California Class 1 type since these nitro compounds are toxic, mobile and slightly volatile. In addition, their solubility of 100 to 150 ppm in water presents a long-term potential hazard to underground water supplies.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Dilute aqueous wastes are best treated on site or in conjunction with municipal sewage treatment systems by conventional biological treatments. Unusable concentrated nitrotoluene and nitrophenol materials are best disposed of by common industrial incineration techniques. Therefore, the nitro compounds discussed in this report are not judged to be candidate waste stream constituents requiring National Disposal Site treatment.

7. REFERENCES

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1492. Merck and Company, Inc. The Merck index of chemicals and drugs. Rahway, New Jersey, 1960. 1,643 p.

1543. Ludzack, F. J., and M. B. Ettinger. Journal Water Pollution Control Federation, 32:1,173-1,200, 1960.

1569. Manual of hazardous chemical reactions. Boston National Fire Protection Association, 1971. 308 p.

2479. Nitrobenzene chemical safety data sheet SD-21, Washington, 1956. 16 p.

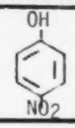
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name p-Nitrophenol (310)

IUC Name 4-nitrophenol

Common Names

Structural Formula



Molecular Wt. 139.1 Melting Pt. 113-114 C(1) Boiling Pt. 279 C (d)(1)

Density (Condensed) 1.270 @ 120/4 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1.6 g/100 ml 25 C(4) Moderate(2) Hot Water 29 g/100 ml 90 C(4) Very(3) Ethanol Very(2)

Others: very, chloroform, ether; addition of base of carbonate to aqueous solutions increases solubility(2)

Acid, Base Properties acidic, $K_a = 7x10^{-8}$

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766 (4) 1433
(2) 1492
(3) 1570

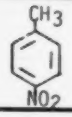
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name p-Nitrotoluene (312)

IUC Name 4-nitrotoluene

Common Names methyl nitrobenzene

Structural Formula



Molecular Wt. 137.1 Melting Pt. 51.9 C(1) Boiling Pt. 238.3 C(1)

Density (Condensed) 1.286 @ Density (gas) 4.72(1) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 53.7 C(1) @ @

Flash Point 223 F(1) Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water very slightly(2) Hot Water Ethanol soluble(2)

Others: soluble, benzene, ether, chloroform, acetone,(2) carbon tetrachloride, carbon disulfide.(3)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification IATA: Poison B, poison label Coast Guard Classification

Comments

References (1) 0766
(2) 1492
(3) 1570

PROFILE REPORT

Oxalic Acid (317)

1. GENERAL

Oxalic acid is the first member of the homologous series of organic, dicarboxylic acids. It is widely distributed in plants, particularly in those of the "Oxalis" and "Rumex" families, where it occurs in the cell sap as the potassium or calcium salt.[1492] The acid is commercially available as the dihydrate, an odorless, crystalline material which is supplied in particle sizes ranging from fine powder to coarse granular.[1433] The principal hazards associated with the dihydrate and the less frequently encountered anhydrous acid and their solutions are a consequence of the acidity of oxalic acid, its volatility and its ability to form insoluble salts.[1492]

There are several synthetic routes for the preparation of oxalic acid,[1433] but only two are in current use by the major, domestic manufacturers.[1506] The acid is manufactured by Allied Chemical, by the heating of sodium formate, in Buffalo, New York (capacity: 10 million lb/year), and Marcus Hook, Pennsylvania (capacity: 10 million lb/year).[1506] Pfizer, Inc. produces the material (capacity 12 million lb/year) in Groton, Connecticut as a by-product of the fermentation process used for the production of citric acid.[1506,1567] Both manufacturing processes require extensive reuse of reaction by-products and recrystallization liquors for economic viability,[1433] thus providing an impetus for control of effluent quality.

Oxalic acid is employed in a variety of applications by organizations ranging in size from small to very large.[1006,1492,1433,1567] Its principal uses and their approximate share of the market are:[1506] textile finishing, stripping and cleaning, 27 percent; metal and equipment cleaning,

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27 percent; chemicals, 25 percent; leather tanning, 2 percent; other (laundry, photography, etc.), 19 percent. There is a gradual trend to replace oxalic acid, in some of its applications, with more innocuous materials.[1567]

The physical/chemical properties of oxalic acid are summarized in the attached worksheet.

2. TOXICOLOGY[0766]

Acute oxalic poisoning results from ingestion of a solution of the acid. There is marked corrosion of the mouth, esophagus and stomach, with symptoms of vomiting, burning abdominal pain, collapse and sometimes convulsions. Death may follow quickly. The systemic effects are attributed to the removal by oxalic acid of the calcium in the blood. The renal tubules become obstructed by insoluble calcium oxalate, leading to massive kidney failure. Inhalation of the dust or vapor may cause symptoms of irritation of the upper respiratory tract and gastrointestinal disturbances.

Toxicological evaluation indicates that the Threshold Limit Value for man is 1 mg/M^3. Toxicity data for species other than man are sparse, but an oral LD in dogs of 1.0 g/kg has been reported.[1492]

3. OTHER HAZARDS

Oxalic acid causes severe contact dermititus typical of strong organic acids.[0766] This acidity is also likely to be manifest by exothermic reactions with concentrated basic substances.

Explosive reactions have been reported for mixtures of oxalic acid with sodium chlorite and sodium hypochlorite.[1569] Since oxalic acid is a reducing agent, care should be taken to preclude its contact with strong, concentrated oxidizing agents.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Care should be taken to avoid inhalation of oxalic acid dust or prolonged skin contact with the acid. Normal, safe industrial practice for the handling of strong acids should provide adequate protection.

Oxalic acid is usually supplied as the dihydrate and packed in fiber drums.[1433] It is classed by the International Air Transport Association as Poison B, requiring a poison label and limited to a maximum of 25 kg on passenger flights and 95 kg on cargo flights.[0766]

Disposal/Reuse

Purification of oxalic acid by recrystallization is a normal part of the manufacturing process[1433] and oxalic acid users with the required equipment may employ this technique to recover slightly contaminated material.

An adequate process for the disposal of oxalic acid must include two important steps. First, the waste must be diluted with water to lower the concentration of oxalic acid to <10 percent (will not cause death if swallowed[1433]) to reduce danger of poisoning, eliminate dust and provide a heat-sink for the second required step; neutralization with base. Salt formation by neutralization eliminates the danger of acid burns and reduces the volatility of the material. The particular base to be used in the neutralization depends on the nature of the final disposal process (Section 5).

Recommended provisional limits for oxalic acid in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Oxalic acid in air	0.01 mg/M^3	0.01 TLV
Oxalic acid in water and soil	0.05 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The preferred processing options for the disposal of oxalic acid wastes are briefly described in the following paragraphs together with judgments as to their adequacy.

Option No. 1 - Incineration

One common method for the disposal of industrial oxalic acid waste is to neutralize it with limestone to form insoluble calcium oxalate which is then incinerated.[1567] This is probably the best method for disposal of oxalic acid since the products of combustion are harmless carbon dioxide and calcium oxide which can be recycled to neutralize more acid waste. The efficient collection of calcium oxide requires either electrostatic or wet collection equipment downstream of the incinerator.

Combustion of oxalic acid without neutralization is not recommended since toxic carbon monoxide and formic acid are among the materials produced. In addition, there is the strong possibility of the release to the atmosphere of some of the volatile oxalic acid.

Option No. 2 - Waste Water Treatment

Effective disposal of oxalic acid by the activated sludge process has been reported.[1543] This process is adequate for waste disposal but is generally more expensive and difficult to operate than incineration (see Waste Disposal Process Descriptions, Volumes III and IV).

Other biological treatments such as aerated lagooning are less acceptable. The soluble salts (potassium or sodium oxalate) that are required for their efficient operation introduce the possibility of drainage into ground water.

In view of the wide range of size and sophistication of the industrial organizations using oxalic acid,[1433,1506] it would not be surprising if some small volume users discard their waste directly into sewer systems and streams. Although not recommended, this practice will not be harmful provided the quantity is small and well diluted since oxalic acid in aqueous solution is decomposed by ultraviolet radiation with the liberation of carbon dioxide.[1433]

Option No. 3 - Land Burial

Many users of oxalic acid neutralize their waste streams with limestone and bury the recovered calcium oxalate in Class 2 landfill or deep wells.[1567] These methods are not generally recommended because of the danger of release of oxalic acid by the leaching action of acidic wastes. Another potential danger lies in inadvertent contact with strong oxidizing agents in the burial area. Disposal in California Class I-type landfills is adequate if strong oxidizing agents are not present.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Oxalic acid does not appear to be a candidate waste stream constituent for disposal at National Disposal Sites. The hazards associated with oxalic acid can be alleviated by the simple process of dilution and neutralization and it can then be effectively and safely eliminated in incinerators equipped with particulate removal devices, or buried in a Clas 1 type landfill.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Oxalic Acid (317)

$C_2H_2O_4$

IUC Name Ethanedioic Acid

Structural Formula

$HO_2C\text{-}CO_2H$

Common Names

Molecular Wt. 90.04(1)

Melting Pt. 189.5 C(1)

Boiling Pt. 157 C(1)(Sublimes)

Density (Condensed) 1.90 @ 17 /4 C(1)

Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

0.92 mm @ 60 C(4)

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility (4)

Cold Water 8.7 g/100 g @ 20 C

Hot Water 54.3 g/100g @ 90 C

Ethanol Very soluble

Others: Ether (anhyd: 23.6 g/100 g, dihydrate 1.47 g/100 g @ 20 C

Acid, Base Properties Strongly acidic (2)

Highly Reactive with Silver, Sodium Chlorite, Sodium Hypochlorite(5)

Compatible with Fiber drums(4)

Shipped in IATA: Poison B, poison label, 25 kg. (passenger), 95 kg (cargo)(2)

ICC Classification

Coast Guard Classification

Comments Normally available as the dihydrate, mp. 101.5 C(loss of H_2O and sublimation)(4)
Mfg(3): Allied Chem, Pfizer.

References (1)	1570	(4)	1433
(2)	0766	(5)	1569
(3)	1506		

PROFILE REPORT

Phosgene (Carbonyl Chloride) (329,101)

1. GENERAL

At ordinary temperatures and pressures, phosgene is a colorless, nonflammable, highly-toxic gas with an odor like that of musty hay. It is readily liquified to a colorless to light yellow liquid and is shipped in steel cylinders as a liquified gas under its own vapor pressure (10.7 psig at 70 F). Phosgene is made by the addition of chlorine to carbon monoxide in the presence of a catalyst, usually carbon granules.

$$CO + Cl_2 \rightarrow COCl_2$$

Because much heat is evolved, the reaction is usually started in a water-cooled reactor and then as the reaction nears completion, the temperature is allowed to rise slightly.[1301] Phosgene is easily separated from the starting materials because it has a much lower vapor pressure than either carbon monoxide or chlorine. The unreacted chlorine and carbon monoxide are recycled.

Phosgene is used in organic synthesis in the manufacture of dyes, pharmaceuticals, herbicides, insecticides, synthetic foams, polymers and as a chlorinating agent (acetyl chloride).[1301] Any unreacted phosgene discharged from a reactor must be treated as discussed in Section 5.

The physical/chemical properties for phosgene are summarized in the attached worksheet.

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2. TOXICOLOGY

Human Toxicity

Phosgene is a highly toxic gas, being over 10 times as toxic as chlorine. Serious symptoms may not develop until several hours after exposure. The immediate symptoms produced by a fatal dose may be relatively mild since phosgene elicits no marked respiratory reflexes. Phosgene is a lung irritant and causes severe damage to the alveoli of the lungs. This is followed by pulmonary edema, resulting in asphyxiation. Its effects are probably due to hydrolysis and the formation of hydrochloric acid inside the body. The most pronounced symptoms of phosgene poisoning are coughing with bloody sputum and weakness which may last for months.

The least detectable odor of phosgene is 5.6 ppm, the least concentration that affects the throat is 3.1 ppm, the least concentration causing irritation of the eyes is 4.0 ppm and the least concentration causing coughing is 4.8 ppm. A concentration of 200 to 500 ppm is lethal to most animals in a few minutes. The median lethal dosage for phosgene (U. S. Army symbol - CG), expressed as a function of exposure time and CG concentration in air, is 3,200 mg - min/M^3.[2442] The effects of phosgene are cumulative. The maximum concentration to which animals can be exposed for several hours without serious symptoms is 0.1 ppm. This is accepted as both the Maximum Allowable Concentration (MAC) for 8-hr exposure, and the Threshold Limit Value (TLV).

3. OTHER HAZARDS

Phosgene does not create a fire or explosion hazard. It is slightly soluble in water and slowly hydrolyzes to liberate hydrochloric acid. When used in dry equipment with anhydrous reagents, it is not corrosive to ordinary metals. In the presence of moisture, corrosion develops in most metals except monel and tantalum. Glass equipment may also be used with moist phosgene.[1301]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Transportation, and Storage

Personnel handling and using phosgene must have available gas masks of a design approved by the U. S. Bureau of Mines for phosgene service with cannisters approved for use with phosgene.

All equipment intended for use in phosgene service must be adequately designed to withstand the pressures to be encountered and be without any leaks.

Phosgene is classified by the Department of Transportation (DOT) and the U. S. Coast Guard as a Class A poison and is shipped under the "Poison Gas" label in steel cylinders up to one ton in size without safety devices. These containers are usually used only for the storage of phosgene and must be stored away from sources of heat to prevent dangerous hydrostatic pressures from developing in the cylinder.

Disposal/Reuse

Phosgene waste is almost always in the form of a dilute gaseous vent stream contaminant, when discharged from the containers or from the reactors in which it is used as a reagent. Recovery and reuse of this vented phosgene is generally economically impractical. The discharged phosgene must be treated by the methods described below. Safe disposal of phosgene is defined in terms of the recommended provisional limits for the atmosphere, and for water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Phosgene	0.004 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis Recommendation
Phosgene	0.02 mg/l	Stokinger and Woodward Method

Contaminated tank car lots of phosgene should, if safe for transportation, be returned to the manufacturer for reprocess and recovery.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processing options for the disposal of phosgene in the gaseous state are briefly described in the following paragraphs, together with recommendations as to adequacy. The Manufacturing Chemist Association[1141] does not publish a recommended method for phosgene disposal, but instead recommends that any unused material be returned to the vendor.

Option No. 1 - Scrubbing With Caustic

Phosgene has been treated by discharging the gas into a scrubbing tower containing 5 percent sodium hydroxide solutions.[1487] However, a discussion with a manufacturer of phosgene[1487] indicated that a packed column containing a solution of sodium hydroxide, potassium hydroxide or ammonia is required. The contact time in the column must be rather long. With adequate attention to dilution (high stacks, forced air, etc.), packed bed scrubbers and towers have been used. Because of the extremely toxic character of phosgene, the existing engineering data is not sufficient to enable design of scrubbing systems with the required safety. It is recommended that additional data be generated to enable design of safe disposal systems for phosgene.

Option No. 2 - Reaction With Alcohols

Phosgene reacts with alcohols to yield first chloroformates and then carbonates. The carbonates have a market for the manufacture of polymers.[1487] This method, if properly performed, allows nearly complete removal of phosgene from a gas stream. However, again adequate details are lacking to enable design of safe systems. Additional work is required to obtain the engineering data necessary to assure complete removal of phosgene.

Option No. 3 - Elevated Temperature Hydrolysis With Steam and Na_2CO_3 Scrubbing

A suggested approach, is reaction with steam at moderately elevated temperatures to yield CO_2 and HCl, followed by sodium carbonate solution scrubbing to remove the HCl. The reactions are as follows:

$$COCl_2 + H_2O \xrightarrow{\Delta} CO_2 + 2\ HCl$$

$$2\ HCl + Na_2CO_{3(aq)} \rightarrow 2\ NaCl_{(aq)} + H_2O + CO_2\uparrow$$

The engineering parameters necessary for design of the hydrolysis system are not available in the literature. The engineering parameters required for design of the HCl scrubbing system are available.

No data is currently available on the $COCl_2$ content of waste streams discharged from the currently used versions of the above three disposal options. Based on engineering principles, the elevated temperature reaction with steam followed by sodium carbonate solution is the preferred option, the reaction with alkali solution in a packed tower is second in preference, and the reaction with alcohol third in order of preference.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that phosgene wastes generated in chemical processes and either excess phosgene or small quantities left in returned cylinders can be handled best at the source of the wastes rather than at a National Disposal Site. However, the necessary design parameters for the disposal method described in Section 5 are lacking. We recommend that a "proof of concept" experiment be performed, and that the necessary engineering data be obtained experimentally.

The "proof of concept" experiments would consist of the reaction of dilute phosgene-airstreams with steam in a carbon-packed, jacketed glass column at various flow rates, initial phosgene concentrations and temperatures. The data obtained by analysis of the effluents would be used in conjunction with thermodynamic data from the literature to derive the equilibrium constants, reaction rate constants, and other engineering parameters needed for safe system design.

7. REFERENCES

1141. Manufacturing Chemists Association. Laboratory waste disposal manual. 2d ed. Manufacturing Chemists Association, Sept. 1969. 14 p.

1301. Matheson Company, Inc. Matheson gas data book. 4th ed. East Rutherford, New Jersey, 1966. 500 p.

1487. Personal communication. Mr. Huff, Chemetron Corporation, to J. R. Denson, TRW Systems, Mar. 27, 1972.

2442. Department of the Army and Air Force. Military chemistry and chemical agents. TM-3-215, AFM-355-7. Washington, Dec. 1963. 101 p.

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Phosgene (101)

IUC Name Phosgene

Common Names Carbonyl Chloride

Structural Formula

$COCl_2$

Molecular Wt. 98.93 Melting Pt. -127.85 C Boiling Pt 7.56 C

Density (Condensed) 1.417g/cc @ 0 C Density (gas) 3.4 @ 20 C

Vapor Pressure (recommended 55 C and 20 C)

1.08 atm @ 10 C 1.55 atm @ 20 C 3.99 atm @ 50 C

Flash Point - Autoignition Temp. -

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Slightly (hydrolyzes) Hot Water hydrolyzes Ethanol reacts

Others: Soluble in benzene

Acid, Base Properties Hydrolyzes in H_2O to give HCl

Highly Reactive with Alcohols, amines

Compatible with In anhydrous form, compatible with most metals

Shipped in steel cylinders, special one ton cylinders

ICC Classification Class A poison Coast Guard Classification Class A poison

Comments

References (1) 1301

PROFILE REPORT

Polychlorinated Biphenyls (507)

1. GENERAL

Polychlorinated biphenyl and polychlorinated polyphenyls range in form and appearance from mobile oily liquids to fine white crystals and hard transparent resins. They are non-oxidizing, permanently thermoplastic, of low volatility, and non-corrosive to metals.[1727]

Aroclor is the registered trademark of Monsanto Company, the sole supplier and manufacturer of polychlorinated biphenyls in the United States.[1726] These materials are obtained when benzene is heated to between 700 and 800 C and the vapor passed through molten lead or hot tubes to form bi- and terphenyls. The bi- and terphenyls are then halogenated to form the Aroclors.[1316]

Polychlorinated biphenyls were produced by Swan Chemical Company in 1929 in response to the electrical industry's need for an explosion proof insulating fluid for transformers. Monsanto acquired Swan in the early thirties and in the same period new applications opened up for polychlorinated biphenyls as industrial heat-transfer media. Monsanto promoted the use of these materials in the 1960's for sealants, chlorinated rubber, adhesive, printing inks and insecticides.[1726] These materials have also been used as a component or extender in elastomers, paints, lacquers, varnishes, pigments and waxes.[1727]

The polychlorinated biphenyls have come under heavy attack from environmental groups and in Congress from Representative William Ryan (Dem., New York) because of their similarity to DDT in their effect on eggs and animal life. As a consequence of this adverse environmental impact, Monsanto is now limiting the sale of polychlorinated biphenyls to applications involving completely closed systems. In effect, insulation of electrical equipment is the only domestic market now permitted for these materials. Monsanto is refunding full payment for unopened drums of material and paying freight costs for the return of opened drums of material to be destroyed in the incinerator at the company's Sauget, Illinois plant.[1660]

General physical properties of the Aroclor chlorinated compounds are found in the attached worksheets.

2. TOXICOLOGY

At ordinary temperatures the polychlorinated polyphenyls have not presented industrial toxicological problems. The hazard of potential toxic exposure increases with increased volatility. Thus, the Aroclors with a lower level of chlorine substitution present more of a potential problem from the standpoint of inhalation even though they may be less inherently toxic than their more highly substituted homologues.

The chlorinated diphenyls have two distinct actions on the body, namely, a skin effect and a toxic action on the liver. The lesion produced in the liver is an acute yellow atrophy. This hepato-toxic action of the chlorinated diphenyls appears to be increased if there is exposure to carbon tetrachloride at the same time. The higher the chlorine content of the diphenyl compound, the more toxic is it liable to be. Oxides of chlorinated diphenyls are more toxic than the unoxidized materials.

The skin lesion is known as chloracne, and initially consists of small pimples and dark pigmentation of the exposed areas. Later, comedones and pustules develop. In persons who have suffered systemic intoxication the usual signs and symtoms are nausea, vomiting, loss of weight, jaundice, edema and abdominal pain. Where the liver damage has been severe, the patient may pass into coma and die.

Inhalation tests on animals indicate that the maximum safe concentration of vapor is in the range of 0.5 to 1.0 milligrams per cubic meter of air for the lower chlorinated Aroclor compounds. The Threshold Limit Value (TLV) (maximum allowable concentration for an 8-hr working day) set by the American Conference of Government Hygienists are 1.0 milligram of the lower-chlorinated Aroclor compounds per cubic meter of air and 0.5 milligrams per cubic meter of air for the more highly chlorinated compounds such as Aroclor 1254.

3. OTHER HAZARDS

There is only a slight fire hazard when chlorinated diphenyls are exposed to heat or flame.[0766] The viscous polyphenyl liquids and resins will not support combustion when heated alone, and they impart fire-reistance to other materials. Continuous repeated skin contact with polychlorinated polyphenyls must be avoided because of the possible occurrence of chlorance. Although reports of this condition caused by these materials are rare, it can be produced by excessive skin contact.[1727]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The polychlorinated polyphenyls are compatible with most metals from room temperature to 125 C. Organic resins show less resistance and detailed information on this subject has been supplied by Monsanto.[1727] Liquid polychlorinated polyphenyls are shipped in steel drums, cans and tank cars. Solid materials are generally shipped in steel drums, fiber drums and bags.[1727] Freight and rail classification for these materials is NOIBN (not otherwise indexed by name). Truck classification is NOI (not otherwise indexed).

Safety in the handling and use of polychlorinated biphenyls required that exposure to the liquids and their vapors be minimized. Workmen must be supplied with proper protective clothing and ventilating systems must be designed and maintained to provide work areas with vapor concentrations below the limits mentioned in Section 2.

Disposal/Reuse[1727]

Monsanto's polychlorinated biphenyl manufacturing operations have experienced a tightening of standards on handling these materials. To prevent water contamination, there is none of the hosing down found in most chemical plants. Other measures include complete monitoring of all vents and traps for leaks at all sample points. All tanks are closed and all of the air and gas that escapes the plant is passed through a Brink mist eliminator. In addition, process temperatures have been lowered to prevent vaporization.

Clothing is provided for all workers, and after the clothes are cleaned all the cleaning fluid is collected for destruction by incineration. The incinerator operates at a temperature of 3,000 F. Hydrochloric acid evolution is prevented by use of a water scrubber and by neutralization of the resulting fluid. Recommended provisional limits for polychlorinated polyphenyl to the environment are as follows:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Lower Chlorinated Aroclors in Air	0.01 mg/M^3	.01 TLV
Higher Chlorinated Aroclors in Air	0.005 mg/M^3	.01 TLV
Lower Chlorinated Aroclors in Water and Soil	0.05 ppm (mg/l)	Stokinger and Woodward Method
Higher Chlorinated Aroclors in Water and Soil	0.025 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Polychlorinated polyphenyls are expected to appear as concentrated[1660] and dilute organic wastes as solids, liquids and vapors.[1726] The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Polychlorinated Biphenyls

Contaminated polychlorinated biphenyls are reprocessed by Monsanto by passing the material through a series of clay filters.[1726] Concentrated materials that cannot be reprocessed in this manner are incinerated at 3,000 F and the effluent gas scrubbed to remove any chlorine containing products.[1661] These are adequate means of disposal/reuse.

Dilute Solid Polychlorinated Biphenyl Wastes

Materials containing polychlorinated biphenyls such as plastics are placed in incinerators at relatively low temperatures for disposal. The polychlorinated biphenyls are not destroyed in this process and may be emitted to the atmosphere. High temperature (3,000 F) incinerators with effluent gas scrubbers (see section on concentrated polychlorinated biphenyls) are also used. The high temperature incinerators are adequate for the disposal of these materials. The low temperature incinerators are not recommended because of incomplete destruction of the polychlorinated biphenyls.

Dilute Liquid Organic Polychlorinated Biphenyl Wastes

Cleaning fluids used to clean work clothes are incinerated as described in the section on concentrated polychlorinated biphenyls. Tars and/or bottoms containing these materials should be disposed of in a similar manner.

Dilute Aqueous Polychlorinated Biphenyl Wastes

Although dilute aqueous wastes have not been identified with polychlorinated biphenyl manufacture, it is recommended that any such waste be concentrated and incinerated as described in the section on concentrated polychlorinated biphenyls.

Dilute Vapor Polychlorinated Biphenyl Wastes

All of the air and gas that escapes the Monsanto plant is passed through a Brink mist eliminator.[1726] This is an adequate means of control provided federal, state and local emission standards are not exceeded.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Polychlorinated biphenyl wastes are expected to appear in both concentrated and dilute forms. Adequate means of handling the disposal of these wastes are located at industrial disposal facilities and represent common industrial technology. Users are encouraged by the manufacturer to return concentrated waste for disposal (see Section 1). Dilute wastes should be treated as discussed in Section 5. These materials are not judged to be candidate waste stream constituents for National Disposal Sites.

7. REFERENCES

0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Company, 1968. 1,251 p.

1316. Noller, C. R. Chemistry of organic compounds. 2d ed. Philadelphia, W. B. Saunders Company, 1957. 978 p.

1660. Hot option for disposal of hydrocarbon wastes. Chemical Week, 110(16):37-38, Apr. 1972.

1726. Pollution cops lot not 'appy. Chemical Week, 108(16):19-20, Apr. 1971.

1727. Monsanto. The Aroclor polychlorinated polyphenyls. Technical Bulletin No. 0-FF/1. St. Louis, Missouri. 24 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated polyphenyls
Aroclor® 1221

Molecular Wt.

Pour Pt. Crystals 1 C

Distillation Range 275-320 C

Density (Condensed) 1.182-1.192 @ 25/15.5 C

@

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point 141-150 C
Cleveland Open Cup

Fire Point. 176 C Cleveland Open Cup

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (mgm. KOH/ gm.) 0.014

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, steel drum, 50-lb can.

ICC Classification NOIBN

Coast Guard Classification

Comments Mfg: Monsanto. Material is a colorless mobile oil

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor® 1232

Molecular Wt.   Pour Pt. -35.5 C   Distillation Range 290-325 C

Density (Condensed) 1.270-1.280 @ 25/15.5 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

5×10^{-3} mm @ 37.8 C   @   @

Flash Point 152-154 C
Open Cleveland Cup   Fire Pt. 238 C Cleveland Open Cup

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water Insoluble   Hot Water   Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/gm.) 0.014

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, 550-lb steel drum, 50-lb can.

ICC Classification   Coast Guard Classification

Comments Mfg: Monsanto. Material is practically colorless mobile oil

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor® 1248

Molecular Wt. Pour Pt. -7C Distillation Range: 340-375 C

Density (Condensed) 1.405-1.415 @ 65/15.5 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

3.3 mm @ 150 C ~3.7×10^{-4} @ 37.8 C @

Flash Point 193-196 C
Cleveland Open Cup
Fire Pt. None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.010

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, 600-lb steel drum, 50-lb. can

ICC Classification NOIBN Coast Guard Classification

Comments Mfg: Monsanto. Material is colorless to light yellow-green, clear mobile oil

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor^{R} 1242

Molecular Wt. Pour Pt. -19 C Distillation Range 325-366 C

Density (Condensed) 1.381-1.392 @ 25/15.5 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

4.3 @ 150 C 1 x 10^{-3} mm @ 37.8 C @

Flash Point 176-180 C - Fire Pt. None
Cleveland Open Cup

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity- maximum (Mgm. KOH/gm.) 0.010

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, 600-lb steel drums, 50-lb can.

ICC Classification NOIBN Coast Guard Classification

Comments Mfg. Monsanto. Material is practically colorless mobile oil

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

Structural Formula

IUC Name

Common Names Polychlorinated Polyphenyls
Aroclor® 1254

Molecular Wt.   Pour Pt. 10 C   Distillation Range. 365-390 C

Density (Condensed) 1.495-1.505 @ 65/15.5 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1.3 @ 150 C   ~6 x 10^{-5} mm @ 37.8 C   @

Flash Point None   Fire Point: None

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water Insoluble   Hot Water   Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/gm.) 0.010

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, 600-lb steel drum, 50-lb can

ICC Classification NOIBN   Coast Guard Classification

Comments Mfg: Monsanto. Material is light yellow viscous oil

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor® 1260

Molecular Wt.   Pour Pt: 31 C   Distillation Range: 385-420 C

Density (Condensed) 1.555-1.566 @ 90/15.5 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

2 mm @ 175 C   @   @

Flash Point None   Fire Pt: None

Flammability Limits in Air (wt %) Lower   Upper

Explosive Limits in Air (wt. %) Lower   Upper

Solubility

Cold Water Insoluble   Hot Water   Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.014

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in Tank car, 600-lb steel drum, 50-lb can

ICC Classification NOIBN   Coast Guard Classification

Comments Mfg: Monsanto. Material is light yellow soft sticky resin

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Common Names Polychlorinated Polyphenyls
Aroclor^R 1262

Structural Formula

Molecular Wt.

Pour Pt: 35-38 C

Distillation Range: 395-425 C

Density (Condensed) 1.572-1.583 @ 90/15.5 C

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point None

Fire Pt: None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble

Hot Water

Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.014

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals.

Shipped in Tank car, 600-lb steel drum, 50-lb can

ICC Classification NOIBN

Coast Guard Classification

Comments Mfg: Monsanto. Material is light yellow sticky clear resin

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor^{R} 1268

Molecular Wt.

Softening Pt: 150-170 C Distillation Range: 435-450 C

Density (Condensed) 1.804-1.811 @ 25/25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point None Fire Pt: None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.05

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in 200-lb fiber drum, 50-lb ca

ICC Classification NOIBN Coast Guard Classification

Comments Mfg: Monsanto. Material is white to off-white powder

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Common Names Polychlorinated Polyphenyls
Aroclor^R 4465

Structural Formula

Molecular Wt.
Softening Pt: 60-66 C
Distillation Range: 230-320 C

Density (Condensed) 1.670 @ 25/25 C
Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point None
Fire Pt: None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble
Hot Water
Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.05

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in 500-lb steel drum, 50-lb can

ICC Classification NOIBN
Coast Guard Classification

Comments Mfg: Monsanto. Material is light-yellow, clear, brittle resin

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name ______________

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor^R 5442

Softening Pt: 46-52 C Pour Pt: 46 C Distillation Range: 215-300 C

Density (Condensed) 1.470 @ 25/25 C Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point 247 C
Cleveland Open cup

Fire Pt: >350 C

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water Insoluble Hot Water ______ Ethanol ______

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.05

Highly Reactive with ______

Compatible with A vareity of solvents, oils and resins, most metals

Shipped in 450-lb steel drum, 50-lb can

ICC Classification NOIBN Coast Guard Classification ______

Comments Mfg: Monsanto. Material is yellow transparent sticky resin

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor^R 5460

Molecular Wt.

Softening Pt: 98-105.5 C Distillation Range: 280-335 C at 5 mm. Hg.

Density (Condensed) 1.670 @ 25/25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point None Fire Pt: None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 0.05

Highly Reactive with

Compatible with A variety of solvents, oils and resins, most metals

Shipped in (Flaked) 100-lb bag

ICC Classification NOIBN Coast Guard Classification

Comments Mfg: Monsanto. Material is clear, yellow-to-amber, brittle resin

References (1) 1727

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polychlorinated Biphenyls (507)

IUC Name

Structural Formula

Common Names Polychlorinated Polyphenyls
Aroclor^{R} 2565

Molecular Wt. Softening Pt: 66-72 C Distillation Range: -

Density (Condensed) 1.734 @ 25/25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point None Fire Pt: None

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble Hot Water Ethanol

Others: Soluble in most common solvents

Acid, Base Properties Acidity-maximum (Mgm. KOH/Gm.) 1.4

Highly Reactive with

Compatible with A vareity of solvents, oils and resins, most metals

Shipped in 500-lb steel drum, 50-lb can

ICC Classification NOIBN Coast Guard Classification

Comments Mfg: Monsanto. Material is black, opaque, brittle resin

References (1) 1727

PROFILE REPORT

Polyvinyl Nitrate (PVN) (535)

1. GENERAL

PVN is an insoluble explosive which is not used because of its poor stability and because it cannot be placed into solution with a solvent.[0474,2169] If used, it would have some of the applications of nitrocellulose. PVN can be prepared by the nitration of polyvinyl alcohol with a mixture of nitric acid and acetic anhydride, or with a mixture of nitric acid and carbon tetrachloride. It is a readily flammable substance which burns without melting.

Since PVN is not manufactured or used, it has not received DOD storage and handling classifications, and shipping regulations covering the material have not been published. If it should be manufactured in the future, shipping, handling and disposal procedures should be similar to those for nitrocellulose (see Profile Report on Nitrocellulose, [534]).

The physical/chemical properties for PVN are summarized on the attached worksheet.

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2. REFERENCES

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2169. Fedoroff, B. T., Encyclopedia of explosives and related items. v 1, Picatinny Arsenal, 1960. 692 p.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Polyvinyl nitrate (535)

IUC Name

Common Names PVN

Structural Formula

$(C_2H_3NO_2)_n$

Molecular Wt. (89)n (1)   Melting Pt. 50 C (1)   Boiling Pt.

Density (Condensed) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water Insoluble(1)   Hot Water   Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification None   Coast Guard Classification None

Comments Explosion temperature 265; has been produced only in the laboratory, for experimental use, because of its instability.

References (1) 0474

PROFILE REPORT

Quinone (365)

1. GENERAL

Quinone is a common name for 1,4-benzoquinone, a yellow, crystalline solid having a characteristic, irritating odor. It is the simplest member of a large family of dioxo derivatives of dihydroaromatic compounds found widely distributed in nature. Both synthetic and naturally occurring quinones are of considerable commercial value as dyes, chemical intermediates, fungicides and drugs.

The principal domestic manufacturer of quinone is the Eastman Chemical Product Division of Eastman Kodak.[1571] The material is manufactured at the Kingsport, Tennessee plant by the oxidation of aniline in the presence of an excess of manganese dioxide and sulfuric acid.[1679] Quinone is steam distilled from the reaction liquor and then purified, by recrystallization, for sale in 50-lb (net) fiber drums. The remaining portion of the oxidation solution is neutralized and filtered. The material obtained from the filtrate, after evaporation, is a technical grade of manganese sulfate called Tecmangam, which is sold for use as a source of available manganese in fertilizers and in animal feed.[1679]

Benzoquinone is an important chemical intermediate in the manufacture of dyes, vitamins, bactericides, insecticides, fungicides,[1687] and, of course, hydroquinone (see Profile Report on hydroquinone [220]). It is also useful as a polymerization inhibitor for unsaturated polyesters and as a tanning agent in the leather industry.[1687] There are a number of other, specialized applications which make use of its oxidizing properties.

2. TOXICOLOGY[0766,1687]

Quinone can cause severe local damage to the skin and mucous membranes by contact with it in the solid state, in solution, or in the form of condensed vapor. Contact may result in discoloration, irritation, erythema, swelling, the formation of papules and vesicles, and after prolonged exposure, necrosis. Repeated exposure to high vapor concentrations may cause a greenish-brown stain or a grayish-white opacity of the cornea. In a few cases there has been an appreciable loss of visual accuity. No evidence has been found for a systemic effect.

The distinctive, irritating odor of quinone provides some measure of warning of its presence in harmful concentrations. Its odor becomes perceptible at or just above 0.1 ppm and is quite definite in the region of 0.15 ppm and irritating at 0.5 ppm.

3. OTHER HAZARDS

Quinone itself does not constitute a fire or explosion hazard; however, if present at the site of a fire or explosion, it may emit toxic fumes when heated.[0766] Care should also be taken to avoid uncontrolled contact with strong reducing agents.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Personnel handling quinone should be familiar with its toxicological properties. Gloves and goggles should be provided for their protection and provisions should be made to keep the atmospheric concentration well below 0.1 ppm of air by volume. A careful medical examination of the eyes is advisable before and during continued exposure to this chemical.[1687]

Disposal/Reuse

Quinone may be purified by recrystallization or by sublimation. Users of this material may employ either technique to recover contaminated quinone if the required equipment is available and if the precautions outlined in the section on handling, storage, and transportation are observed.

An adequate process for the disposal of quinone must take into account that it: (1) is toxic as a vapor, or a solid, or in solution; (2) has a high sublimation pressure; (3) is soluble in water; (4) is resistant to biochemical attack because of its toxicity to lower organisms and its high oxidation state. These properties favor disposal processes which provide for control of vapor emission and rapid, complete conversion to innocuous products. Alternatively, quinone may be converted (e.g., by reduction) to less volatile and/or more easily degraded forms before final disposal.

Recommended provisional limits for quinone in the environment are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
Quinone in air	0.001 ppm (0.004 mg/M^3)	0.01 TLV
Quinone in water and soil	0.02 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The preferred processing options for the disposal of quinone wastes are briefly described in the following subsections together with judgments as to their adequacy.

Option No. 1 - Incineration

Incineration in a properly designed and operated incinerator is recommended as the most satisfactory method for the disposal of waste quinone. It is necessary that the incinerator be designed to burn the quinone completely (minimum of 1,800 F for at least 2.0 seconds) and that leackage of unburned quinone vapors be eliminated. This option is applicable to both concentrated and dilute quinone wastes provided that an appropriate incineration method is used.

Option No. 2 - Waste Water Treatment

Biochemical waste water treatment processes are less satisfactory than incineration for the disposal of quinone waste streams. Quinone is toxic to most microbiota, is relatively resistant to oxidation since it is itself an oxidizing agent, and is sufficiently volatile to be a potential odor and toxicity problem in open lagoons. Treatment by the activated sludge process using well acclimated seed is the most satisfactory biochemical treatment method for chemically unmodified quinone wastes.

Quinone wastes can be rendered significantly more biodegradable by prior reduction to hydroquinone or a hydroquinone derivative. Sodium sulfite and sulfur dioxide are suitable reducing agents.[1433] Reduction to hydroquinone, in addition to providing a more easily destroyed compound, also eliminates the problems posed by the volatility of quinone.

Option No. 3 - Land Burial

Land burial disposal processes are generally less satisfactory than Options Nos. 1 and 2 for disposal of quinone wastes. The high sublimation pressure of this material poses the threat of release of toxic quinone fumes to the atmosphere. Another possible route to environmental contamination is the leaching of this water soluble material by rain or liquid wastes. A properly located and operated burial facility meeting California Class I requirements may limit the impact of leaching but is unlikely to completely eliminate the danger of sublimation.

Reduction of the quinone to hydroquinone prior to burial reduces its potential for environmental damage (Option No. 2). However, since hydroquinone is readily oxidized to quinone, the improvement must be regarded as temporary.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Quinone does not appear to be a candidate waste stream constituent requiring disposal at National Disposal Sites. This material is currently effectively and safely disposed of at or near the sites of waste generation using the methods cited in Section 5.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Quinone (365)

IUC Name 1,4-Benzoquinone

Common Names para-Quinone, p-benzoquinone, 1,4-cyclohexadieneone, chinone

Structural Formula

OC_6H_4O

Molecular Wt. 108.10 Melting Pt.(1) 115.7 C Boiling Pt.(2) Sublimes

Density (Condensed)(1) 1.318 @ 20 C/4 C Density (gas) ______ @ ______ ______

Vapor Pressure(4) (recommended 55 C and 20 C)

98 mm @ 25 C ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility (4)

Cold Water 1 g/100g solv. @ 25 C Hot Water ______ Ethanol 6g/100g solv. @ 25 C

Others: Acetone (36g), Ethyl acetate (18g), Benzene (18g)

Acid, Base Properties Neutral

Highly Reactive with Reducing agents

Compatible with ______

Shipped in 50-lb fiber drums(4)

ICC Classification ______ Coast Guard Classification ______

Comments Volatile with steam(2), sources:(3) Eastman Chemical Products, Orlex Dyes and Chemicals Corporation

References (1) 1492 (4) 1687
(2) 1433
(3) 1571

PROFILE REPORT

Tetraethyl- and Tetramethyllead (425,427)

1. GENERAL

Tetraethyllead (TEL) and tetramethyllead (TML) are colorless, oily liquids of very high toxicity. Individually and in mixtures they constitute the major gasoline antiknock agents now in use. More stringent exhaust emission standards are expected to reduce their predominance as gasoline additives.[1506] They are commonly believed to be the major source of environmental lead pollution and they are likely to interfere with the operation of the automobile antipollution equipment that will be necessary to meet future exhaust emission requirements.

Although many synthetic schemes for the preparation of TEL and TML have been disclosed in the technical and patent literature, there are only two basic processes in domestic, commercial use.[1433] By far the more important of the two involves the reaction of sodium-lead alloy with ethyl or methyl chloride as shown in Equation 1. Upon completion of the reaction, the TEL or TML is steam distilled to remove it from the other products. The organolead compounds are then purified by washing with dilute solutions of oxidizing agents (e.g., hydrogen peroxide, sodium dichromate) and then with water. After purification, the TEL and TML are usually mixed with the other ingredients that make up the antiknock fluid and with an identifying dye. The compounded fluid is then pumped into tank cars or bulk-storage tanks. This process, in several modifications, is used by Du Pont (Antioch, California, and Deepwater, New Jersey), Ethyl Corporation (Baton Rouge, Louisiana and Houston, Texas) and Houston Chemical (Beaumont, Texas) with a combined capacity (1971) of 790 million lb per year.[1506]

$$1\ NaPb + 4\ C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 3\ Pb + 4\ NaCl \qquad (1)$$

Nalco Chemical (Freeport, Texas) uses an electrolytic process for TML, based on the electrolysis of a solution of methylmagnesium chloride and excess methyl chloride in an ether solvent, with lead metal acting as the anode.[1433] The overall electrolytic reaction is shown in Equation 2. The capacity of the Nalco plant is 40 million lb per year.[1506]

$$2\ CH_3MgCl + CH_3Cl + Pb \rightarrow (CH_3)_4Pb + 2\ MgCl_2 \tag{2}$$

TEL and TML are also available for use in antiknock fluids as mixtures of organolead compounds produced by a redistribution reaction of mixtures of TEL and TML in the presence of Lewis-acid catalysts (Equation 3).[1433] The production capacity for the redistributed mixtures is included in the total 830 million lb per year capacity cited above.[1506]

$$Me_4Pb + Et_4Pb \rightarrow Me_4Pb + Me_3EtPb + Me_2Et_2Pb + MeEt_3Pb + Et_4Pb \tag{3}$$

The only nonantiknock use for TEL and TML of commercial importance is in the preparation of organomercury fungicides,[1433] another group of materials under investigation as a possible environmental danger.

The physical/chemical properties of TEL and TML are summarized in the attached worksheets.

2. TOXICOLOGY[0766, 1433]

Tetraethyl- and tetramethyllead are extremely toxic materials. Acute or chronic poisoning may result from ingestion, inhalation or absorption through skin. Overexposure to TEL or TML severely affects the central nervous system. The initial symptoms are weakness, nervousness, severe constipation and colic-like pains. Heavy or prolonged exposure may result in death.

The American Conference of Government and Industrial Hygienists has recommended Threshold Limit Values (TLV's) for TEL and TML of 0.10 mg/M^3 and 0.15 mg/M^3 (as Pb) respectively.

3. OTHER HAZARDS

Tetraethyl- and tetramethyllead are considered to be fire hazards when exposed to heat and flame.[0766] The hazardous nature of a fire involving these materials is substantially increased by the danger of exposure to the toxic fumes of TEL, TML, and their decomposition products.

These organolead compounds are also known to react exothermically with halogens, mineral acids and oxidizing agents.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The most significant potential for exposure to TEL and TML occurs in the manufacture of the compounds and their blending into gasoline at the refinery.[1433] Subsequent to the blending operation at the refinery, exposure to these materials is limited by the low concentration in gasoline (less than 4 ml/gal.) and the normal methods of handling the fuel at service stations.

In the manufacturing and blending operations emphasis has been placed on eliminating vapor, dust and liquid leaks.[1433] Adequate exhaust ventilation must be provided in all work areas to maintain the concentration of TEL and TML vapors well below the recommended Threshold Limit Values (TLV) of 0.10 mg/M^3 and 0.15 mg/M^3 (as Pb) respectively. Personnel likely to contact these materials in concentrated form should be provided with proper protective gloves and be made thoroughly cognizant of the danger they pose.

Regular medical examinations should be an integral part of a program to guard against the danger of lead intoxication.[1433] The medical examination should include a urine or, preferably, a blood test to monitor the level of lead in the worker's body. The mean normal lead concentration in whole blood is said to be 0.03 mg/100 cc and in urine a concentration of 0.03 mg of lead per liter is considered normal.[1433]

TEL and TML are generally stored and shipped in steel vessels. Accidental spills which occur in handling or transport can be decontaminated by reaction of the lead compound with dilute potassium permanganate or bromine solution.[1433]

Both of these tetraalkyllead compounds are classified by the Department of Transportation (DOT), Coast Guard and IATA as Poison B, requiring a poison label. The IATA does not permit their shipment on passenger flights and limits cargo flights to a maximum of 220 liters.[0766]

Disposal/Reuse

The recovery and reuse of lead and lead compounds is an integral part of the manufacture of TEL and TML.[1433] Only 25 percent of the lead in the NaPb alloy (see Equation 1) is utilized on each pass through the process. It is a matter of economic necessity that the excess lead be recovered, purified and returned to the process.

Tetraethyl- and tetramethyllead wastes are most likely to appear as dilute aqueous solutions generated in their manufacture,[1046] and as components of the sludge and scale which collect in plant and refinery storage and mixing facilities.[1788]

The adequate treatment of the waste requires that the hazards involved in handling these toxic materials be reduced, that their concentration in effluent aqueous streams be at acceptable levels (<1 ppm[1787]), and that the lead-containing compounds removed from the wastes be converted to forms suitable for reuse. All of those requirements can be met by the conversion of the organic lead compounds to inorganic lead compounds. The inorganic materials can be more easily removed from solution and reduced to metallic lead in a smelting operation. Other advantages of the organic to inorganic conversion accrue by virtue of lessened volatility and reduction of the high lipoid solubility of the organic materials (responsible for their ease of absorption through the skin).[0766]

The recommended provisional limits for tetraethyl- and tetramethyllead in the environment are as follows:

Concentration and Environment	Provisional Limits	Basis of Recommendation
TEL in air	.0010 mg/M^3 as Pb	0.01 TLV
TML in air	.0015 mg/M^3 as Pb	0.01 TLV
TEL in water and soil	0.05 ppm (mg/l) as Pb	Drinking water standards
TML in water and soil	0.05 ppm (mg/l) as Pb	Drinking water standards

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The processes currently employed for the disposal of tetraalkyllead wastes are all basically the same, differing only in detail as dictated by the location and nature of the waste generation source.

Current Disposal Processes

Dilute, aqueous solutions of organic lead compounds generated in the manufacturing process are the major type of TEL and TML wastes. The contaminated water is produced during steam distillation, washing, purification and maintenance operations.[1046] The aqueous wastes are collected in settling pits to recover lead and insoluble lead salts.[0534] The water from the settling pits is then treated to adjust its pH to 8 to 9.5 in the presence of precipitating agents such as ferrous sulfate or sodium carbonate.[0534, 1046] Precipitated lead salts are recovered for recycling to lead metal,[1786, 1787] and the water is allowed to return to the environment.

Despite the ubiquity of the disposal method described above, it is now generally agreed that it does not reduce the lead concentration in effluent streams to acceptable levels. In view of the inadequacy of the current disposal process, the DuPont plant in Antioch, California has been forced to store its lead-containing wastes pending the completion of an incineration facility to convert them to a form more amenable to recycle by lead smelters.[1787] The problem of lead recycling is especially complicated at the Antioch plant, which uses a continuous rather than batch TEL synthesis.[1787]

The Baton Rouge plant of the Ethyl Corporation has also experienced difficulty in maintaining acceptably low lead effluent concentrations.[1786] They are pursuing conventional (unspecified) methods of reducing those concentrations.

The scale and sludge which form in TEL and TML storage, mixing and transport vessels are another source of tetraalkyllead waste. The former practice of dumping the old tanks containing lead residues at sea is no longer used.[1787, 1788] The lead sludges are buried or sold to secondary smelters for recycle.[1788] Petroleum refineries follow the practice of exposing the sludges to the air (weathering) until they are "inactive," after which they are landfilled.[1788] Presumably, the weathering process results in the slow oxidation of the lead compounds to insoluble PbO. However, it seems likely that the evaporation of toxic organic lead compounds cannot be avoided in this essentially uncontrolled exposure and that this method may result in local atmospheric organic lead pollution. This method of disposal is not adequate.

Near Future Disposal Processes

The disposal processes outlined in the following subsections do not appear to be in actual use at this time. They are currently under development or have been reported in the literature.

Option No. 1 - Incineration. An incineration process to convert organic and inorganic lead wastes to PbO for recycle to lead metal is now under development.[1787] The use of this or a similar process for treatment of TEL and TML waste streams is recommended as the most desirable method of reducing their deleterious effects on the environment. An acceptable lead waste burning installation must be fitted with efficient scrubbing devices to prevent the contamination of stack effluents with toxic lead or lead-containing particulates and/or vapors.

Option No. 2 - Ion Exchange. Strongly acidic cation exchange resins have been shown to effect almost complete removal of organic lead compounds from typical TEL aqueous waste streams.[1046] The inorganic lead compounds were removed by conventional means before the stream was introduced to the ion exchange column and the final concentration of lead in the effluent water was less than 1 ppm. After elution from the column with caustic soda the eluate was subjected to oxidative chlorination, affording almost complete conversion to recoverable inorganic lead compounds. Although a judgment with respect to economic practicality of this process is not possible with the data in hand, the removal of organic lead compounds from TEL wastes with ion exchange resins appears to be technically attractive. A complete disposal system incorporating this process must also provide for rendering the inorganic lead obtained suitable for conversion to metallic lead.

Option No. 3 - Improved Precipitation Methods. A number of methods designed to improve the removal of lead-containing compounds from TEL and TML aqueous wastes are now under study.[1787] One such method involves the treatment of aqueous effluents from tetraalkyllead manufacture by: (1) adjusting the pH of the effluent to between 8.0 to 9.5; (2) intimately contacting the aqueous effluent with an ozone-containing gas in the presence of a soluble carbonate; (3) precipitating the converted inorganic lead compounds; and (4) separating the precipitated compounds.[0534] Reduction of the dissolved organic lead content to below 5 ppm is claimed.[0534] Any improved precipitation should be coupled to a process for conversion of the precipitated lead compounds to metallic lead for reuse.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Aqueous tetraethyl- and tetramethyllead waste streams are not candidates for disposal at National Disposal Sites. The aqueous, organolead wastes are generated at six manufacturing facilities belonging to relatively large, sophisticated chemical firms. Although these wastes are not currently treated in a completely acceptable manner, the problems are under intensive study and appear to be amenable to solution by the application of existing technology.

The lead-containing sludges and scales formed in TEL and TML storage, transportation and mixing vessels present a more complicated problem. Their sources are both more numerous and more diverse than those of the aqueous wastes, ranging in size and sophistication from major oil refineries to local, owner-operated service stations. Many of these purveyors of tetraalkyllead-containing gasolines will be unable to dispose of sludge and scale wastes in an acceptable manner. Therefore, the lead-containing sludges and scales may represent a class of materials that could be profitably sent to National Disposal Sites for treatment by incineration and subsequent recycle to metallic lead.

Another, perhaps controlling factor that must be considered with regard to the applicability of tetraalkyllead wastes to National Disposal Sites is the probable diminishing use of these compounds as gasoline additives.[1506] A governmental decision to ban the use of the lead antiknock compounds in gasoline may render the question of the disposal of their wastes academic.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tetraethyllead (425)

IUC Name Tetraethyllead

Common Names Lead tetraethyl, TEL

Structural Formula

$(CH_3CH_2)_4Pb$

Molecular Wt. 323.44 Melting Pt.(1) -136.8 C Boiling Pt.(1) 200 C (d)

Density (Condensed)(2) 1.6528 @ 20 C/4 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.47 mm @ 20 C[2] 2.5 mm @ 55 C(2) 19 mm @ 91 C(1)

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility (1)

Cold Water Insoluble Hot Water Ethanol sl. sol.

Others: Benzene, ether, gasoline

Acid, Base Properties

Highly Reactive with Oxidizing agents;(3) acids and halogens(2)

Compatible with

Shipped in Steel

ICC Classification(3) Poison B Coast Guard Classification Poison B

Comments Begins to decompose at or above 100 C(2)

Sources:(4) DuPont, Houston Chemical Corp., Nalco Chemical, Ethyl Corp.

References (1) 1570 (4) 1718

(2) 1433

(3) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tetramethyllead (427)

IUC Name Tetramethyllead

Common Names Lead tetramethyl, TML

Structural Formula

$(CH_3)_4Pb$

Molecular Wt. 267.33 Melting Pt.(1) -27.5 C Boiling Pt.(1) 110 C

Density (Condensed)(2) 1.9952 @ 20 C/4 C Density (gas)(3) 9.2 @

Vapor Pressure(2) (recommended 55 C and 20 C)

22.5 mm @ 20 C 116.6 mm @ 55 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility(1)

Cold Water Insoluble Hot Water Ethanol sl. sol.

Others: benzene, ether, gasoline

Acid, Base Properties

Highly Reactive with Oxidizing agents;(3) acids and halogens(2)

Compatible with

Shipped in Steel

ICC Classification(3) Poison B Coast Guard Classification(3) Poison B

Comments Sources(4): DuPont, Nalco Chemical, Ethyl Corp.

References (1) 1570 (4) 1718
(2) 1433
(3) 0766

PROFILE REPORT

Tetranitromethane (428)

1. GENERAL

Tetranitromethane is a very toxic colorless liquid that melts at 13 C. It has been used as a rocket propellant, as either oxidizer or monopropellant. At present, its chief use is as an additive to racing car fuels. A minor use is a reagent in a qualitative test for unsaturated compounds.[1486] Tetranitromethane is prepared by reacting acetic anhydride with anhydrous nitric acid.[1485] Manufacture and sales are limited to one company, Hummel Chemical Company.[1411]

Procedures for adequate handling, storage and transportation are not well documented in the published literature. In general, tetranitromethane can be handled in equipment fabricated from most common metals except copper or copper alloys. Fluorocarbon and silicon-based lubricants can be used, but not petroleum-based lubricants. Teflon, polyethylene, butyl rubber and silicone rubber are all compatible with tetranitromethane.[1142] It is shipped as an oxidizing material requiring a yellow label.[0766]

2. TOXICOLOGY

Tetranitromethane irritates the eyes and respiratory passages and does damage to the liver. It appears as an impurity in crude TNT and is thought to be the cause for the irritating properties of that material. It can cause pulmonary edema, mild methaemoglobinemea and fatty degeneration of the liver and kidneys. Animal experiments indicate that concentrations as low as 0.1 ppm have proved rapidly fatal. Concentrations of 3.3 to 25 ppm produce rapid and marked irritation of mucous membranes of the eyes, mouth and upper respiratory tract. The Threshold Limit Value (TLV) recommended by American Conference of Governmental Industrial Hygienists (ACGIH) is 1 ppm.[0766]

3. OTHER HAZARDS

When shocked or exposed to heat, tetranitromethane can explode. It can form a powerful explosive when mixed with other nitrocompounds that are oxygen deficient or with low molecular weight hydrocarbons, benzene, or highly unsaturated hydrocarbons.[1486] When tetranitromethane is burned, visible plumes of oxides of nitrogen are liberated, and a small concentration (part per million range) of hydrogen cyanide is present in the combustion products. There are no reports on measurements of concentrations or quantities of these toxic combustion products.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Adequate procedures for the safe handling and storage of tetranitromethane are described in the JANAF Propulsion Committee's Chemical Rocket Propellant Hazards publication.[1142] Tetranitromethane is classified by the Department of Transportation (DOT) as an oxidizing material and is shipped under a yellow label.[0766]

The safe disposal of $C(NO_2)_4$ is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Tetranitromethane	0.08 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Tetranitromethane	0.4 mg/l	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Tetranitromethane does not present a waste management problem, because only small quantities are produced with a more than adequate market in blending fuels for race cars. The manufacturer, Hummel Chemical Company, will buy back for recycle any excess tetranitromethane in storage.[1486] If it becomes necessary to dispose of excess or contaminated tetranitromethane, the procedure recommended by JANAF Hazards Working Group[1142] for liquid nitro compounds is presumably followed. The procedure calls for open burning, and may be summarized as follows: Tetranitromethane, collected or stored in drums, cans or carboys, is destroyed by open burning at remote burning sites. Container tops or drum bungs are removed, combustible material carefully placed around the containers (avoiding any spillage) and the tetranitromethane is ignited with a black powder squib. This procedure is not entirely satisfactory, since it makes no provision for the control of the toxic effluents, NO_x and HCN. Suggested procedures are to employ modified enclosed pit burning, using blowers for air supply, and passing the effluent combustion gases through loosely packed earth (as an adsorbent), or through wet scrubbers. (Described in detail as a combustion process system for disposal of hazardous wastes). No engineering data on tetranitromethane combustion product characteristics is available for use in design of modified enclosed pit burning systems.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because there is little probability that tetranitromethane in other than laboratory reagent quantities will require disposal, it is our conclusion that this material is not a candidate waste stream constituent for National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tetranitromethane (428)

IUC Name

Common Names

Structural Formula

$C(NO_2)_4$

Molecular Wt. 196.04 (1) Melting Pt. 12.5 C (1) Boiling Pt. 125.7 C (1)

Density (Condensed) 1.650 @ 13 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

10 torr. @ 22.7 C 14.9 torr @ 30 C 25.8 torr @ 40 C

Flash Point 129 C Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water insoluble Ethanol miscible

Others: soluble in ether

Acid, Base Properties

Highly Reactive with reducing substances (explosive); KOH in alcohol.

Compatible with most common metals, except copper and copper-base alloys

Shipped in

ICC Classification Yellow label Oxidizing Material Coast Guard Classification Yellow label Oxidizing Material

Comments

References (1) (0766)

PROFILE REPORT

Tricresyl Phosphate (440)

1. GENERAL

Introduction

The common grades of tricresyl phosphate (TCP) are a mixture of ortho-, meta-, and para- or meta- and para-isomers. It was designated as a probable candidate waste stream constituent for industrial disposal because it is a relatively high volume commodity chemical which has well-defined and safe methods of industrial handling and disposal.

Manufacture/Use[1501,1506]

Tricresyl phosphate is manufactured from equivalent amounts of technical cresol with a minimum amount of o-cresol, and phosphorus oxychloride by a continuous or batch process. Reaction temperatures range from 150 to 300 C and reaction times from 6 to 9 hours. Hydrogen chloride is removed continuously during the reaction by purging with an inert gas or maintaining the reactor under vacuum.

$$3\ CH_3C_6H_4OH + POCl_3 \longrightarrow (CH_3C_6H_4O)_3PO + 3\ HCl$$

The crude material is washed with hot sodium hydroxide (2%) to remove residue hydrochloric and phosphoric acids, cresol and other impurities, and it is given a final water wash. The material is suitable for use in functional fluids and lubricant additives (45%). A refined grade for use as a plasticizer and flame retardant (45%) is produced by vacuum distillation. For certain applications, trace amounts of cresol are removed by treating the refined material with alkaline permanganate, activated charcoal or zinc and acid.

Air filtration media (4%) and miscellaneous applications account for the remainder of the uses. TCP has been replaced as a gasoline additive.

Major manufacturers and plant sites are:[1501,1718]

FMC Corporation; Nitro, West Virgina
Frontier Chemical Corporation; Newark, NewJersey
Monsanto Company; St. Louis, Missouri
Stauffer Chemical Company; Point Pleasant, West Virgina

Physical and Chemical Properties

The physical and chemical properties of TCP are discussed in the attached worksheets.

2. TOXICOLOGY[0766]

Most cases of tricresyl phosphate poisoning have followed ingestion, but poisoning by inhalation or skin absorption is also possible. There have been several mass outbreaks of poisoning due to adulteration of food or drink with TCP or the addition of lubricating oils containing TCP to edible cooking oils.

Early symptoms of actual poisoning are transient gastrointestinal upset, nausea, vomiting, diarrhea and abdominal pain. These are followed in one to three weeks by degeneration of the peripheral motor nerves which is manifested by soreness of the lower leg muscles and "numbness" of the toes and fingers. This is followed in a few days by weakness of the toes and bilateral wrist-drop. More serious poisoning causes further paralysis and even death by damage to the central nervous system. Sensory changes are completely absent. Recovery is slow and the degree of residual paralysis depends on the degree of poisoning. The order of toxicity for the three isomers is ortho, meta, para. The Threshold Limit Value (TLV) is 0.1 mg/M^3.

3. OTHER HAZARDS

The fire hazard of TCP when exposed to heat or flame is slight, but incomplete combustion or heating to decomposition results in the emission of highly toxic oxides of phosphrous.[0766]

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation

Tricresyl phosphate is a non-volatile, non-corrosive and only slightly flammable liquid that is shipped under no special Department of Transportation (DOT) or IATA regulations.[0766,2351] It is a bulk chemical and is most commonly sold in 1- and 5-gal. metal cans, 55-gal. drums, tank trucks, and tank cars.[2400] Standard safety practices should be observed for storage.[0766]

TCP can be absorbed by the body by inhalation or through the skin, and good ventilation should be provided in areas where mists or aerosols may be present. Protective clothing is recommended where necessary. In cases of accidental contact, all contaminated clothing should be removed immediately and the skin washed thoroughly with soap and water.[0766]

Disposal

The manufacture of TCP results in waste material in the form of semi-solid distillation bottoms which are presently disposed of by landfill. Another byproduct of manufacture is a very dilute aqueous stream (20 ppm) of TCP.[1492] This stream also contains high (100 ppm or more) concentrations of cresol and other phenolics and is best considered in the Profile Reports on cresol (124) or phenol (327).[1501]

Tricresyl phosphate with a low content of the ortho-isomer is used as plasticizer for polyvinyl chloride and acetate polymers and cellulose plastics. It is also used as a flame retardant in polyester, polyurethane and polyvinyl chloride plastics. Items made from these plastics are used in thousands of applications.[1433,2400] Practically none are reused, but disposed of with municipal wastes, either by landfill or incineration.[0690,0604]

TCP is also used as an anti-wear additive in conventional hydrocarbon lubricants as well as an important constituent in special lubricants and hydraulic fluids.[1433] Used, out-of-date, or contaminated fluids are not reprocessed and are usually disposed of by landfill.[0590,0604]

The recommended provisional limits for TCP in the environment are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
TCP	0.001 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
TCP	0.005 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Municipal Disposal of Plastic Material Containing Tricresyl Phosphate

Tricresyl phosphate is used as a plasticizer and flame retardant in the thousands of products that are presently disposed of by municipal landfill and incineration activities. TCP can be destroyed with proper incineration. This is adequate as long as phosphorus oxide emissions are not significant. Its low solubility in water (20 ppm)[1492,2400] and great affinity for plastics makes the danger due to underground water leaching very small. It is recommended, however, that the bulk concentration in soil of TCP in any form be maintained below 0.005 ppm.

Option No. 2 - Landfill of Heavy Distillation Bottoms from Manufacture

Refined TCP is produced by distilling technical material under vacuum. The chemical composition of the distillation bottoms is similar to TCP but of higher molecular weight. Landfill of concentrated TCP wastes is recommended only in sites meeting California Class 1 standards.

Option No. 3 - Landfill of Contaminated or Used Hydraulic and Lubricating Fluids

TCP is used as a lubricant and hydraulic fluid additive as well as being a major constituent in many synthetic lubricants and special purpose liquids. In these applications, small amounts are used at many scattered sites. These fluids are periodically changed due to breakdown, contamination, equipment failure or routinely in critical applications. Their exact fate is not known but it is generally thought that most material is landfilled at local municipal sites. The small amounts landfilled from this source along with the low solubility of TCP (20 ppm)[1492,2400] probably presents no excessive long-term hazard to underground water supplies. As mentioned previously, however, TCP bulk soil concentration should be maintained below 0.005 ppm.

Option No. 4 - Recycling of Spent Fluids Containing Tricresyl Phosphate

Although it is only partially feasible at present, the best method of disposal of fluids containing TCP is by recycling or downgrading the application. In applications that require very high standards, such as, aircraft fluids, the fluids are changed regularly for safety reasons. Also, unused fluids are often discarded because of prolonged storage. Although these materials are unsuitable for aircraft applications, they may still be premium fluids for applications requiring lesser standards. Other fluids which have been slightly degraded might be reprocessed to upgrade them for reuse.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

All of the wastes generated in relation to the production and use of TCP can be treated either by industrial and municipal methods such as landfill and incineration. TCP is not judged to be a candidate waste stream constituent requiring National Disposal Site treatment.

7. REFERENCES

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1501. Faith, W. L., D. B. Keyes, and R. L. Clark. Industrial chemicals. 3d ed. New York, John Wiley and Sons, Inc., 1965. 824 p.

1506. Oil, paint and drug reporter profiles. New York, Schnell Publishing Company, Inc., 1970.

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2351. Baskin, A. D. Handling guide for potentially hazardous commodities, Chicago Railway Systems and Management Association, 1972.

2400. Product data sheet for tricresyl phosphate. New York, Stauffer Chemical Company. 2 p.

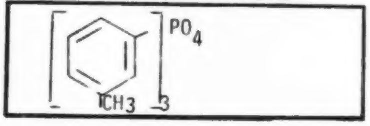
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Trycresyl phosphate (440)

IUC Name tri-3-tolyl phosphate

Common Names

Structural Formula



Molecular Wt. 368.37 Melting Pt. 25-26 C$^{(1)}$ Boiling Pt. 258-263 C (4 mm)$^{(1)}$

Density (Condensed) 1.150 @ 25 C$^{(1)}$ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

≃ 4 mm @ 260 C$^{(1)}$ @ @

Flash Point 410 C$^{(2)}$ Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble$^{(1)}$ Hot Water <20 ppm at 85 C$^{(2)}$ Ethanol slightly$^{(1)}$

Others: soluble ether,$^{(1)}$ most organic solvents.$^{(2)}$

Acid, Base Properties neutral

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766
(2) 1492

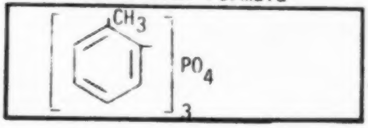
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tricresyl phosphate (440)

IUC Name tri-2-tolyl phosphate

Common Names o-tolylphosphate

Structural Formula



Molecular Wt. 386.34 Melting Pt. -25 to -30 C(1) Boiling Pt. 410 C(1)

Density (Condensed) 1.17 @ 20 C Density (gas) 12.7(1) @

Vapor Pressure (recommended 55 C and 20 C)

17 mm @ ≥ 270-275 C(2) @ @

Flash Point 437 F(1) Autoignition Temp. 725 F(1)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water Ethanol slightly

Others: soluble-ether, chloroform, benzene(3) slightly-hexane, ligroin(3)

Acid, Base Properties neutral

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0766

(2) 1501

(3) 1570

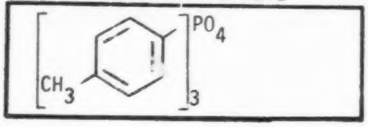
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tricresyl phosphate (440)

IUC Name tri-4-tolyl phosphate

Common Names

Structural Formula



Molecular Wt. 368.37   Melting Pt. 77-78 C(1)   Boiling Pt. 244 C (3.5 mm)(1)

Density (Condensed) 1.247 @ 25 C(1)   Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

3.5 mm @ 244 C(1)   ____ @ ____   ____ @ ____

Flash Point 410 C(2)   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water <20 ppm(2)   Hot Water <20 ppm at 85 C(2)   Ethanol slightly(1)

Others: soluble ether, chloroform, benzene,(1) most organic solvents.(2)

Acid, Base Properties neutral

Highly Reactive with

Compatible with

Shipped in

ICC Classification ____   Coast Guard Classification ____

Comments

References (1) 0766

(2) 1492

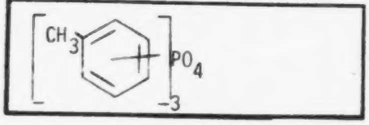
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Tricresyl Phosphate* (440)

IUC Name tritolyl phosphate

Common Names TCP, Lindol, Celluflex, Kronitex, Phosplex

Structural Formula



Molecular Wt. 368.36 Pour Pt. -28 C(1) Boiling Pt. ≃ 265 C(10mm)(1)

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point 455 C(3) Autoignition Temp. 655 C(3)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water <<0.002% Hot Water <.002% at 85 C(1) Ethanol

Others: miscible with all common organic solvents(1)

Acid, Base Properties neutral, commercial material may have traces or cresol.

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments *Commercial material is a mixture of the three isomeric tritoyl phosphates, usually excluding as much as possible of very toxic *ortho*-isomer.(1) Decomposes to highly toxic fumes of phosphorus oxides.(2)

References (1) 1492
(2) 0766
(3) 2400